

PREFACE

The widespread use of synthetic polymers has led to the development of a considerable number of analytical tools for polymer characterization and analysis. Analytical pyrolysis, consisting of pyrolysis coupled with an analytical technique, is one of these tools. The technique can be invaluable in solving many practical problems in polymer analysis. It can be used alone or can provide complementary information to other techniques such as thermal analysis, infrared spectroscopy, or even nuclear magnetic resonance.

The applications of analytical pyrolysis to synthetic polymers range from polymer detection and characterization to the microstructure elucidation of specific polymers and the identification of additives present in polymers (antioxidants, plasticizers, etc.). These applications cover analysis of thermoplastics, fibers, paints, adhesives, and elastomers for quality control characterization, competitor product evaluation, identification of unknown materials, polymer identification for forensic purposes, etc. A subject of major interest in many practical applications regarding polymer properties is the degradation of polymers during heating. Incomplete burning of common objects made from plastics, fibers, or elastomers, with pyrolysis around the combustion area, generates pyrolysates that can have complex compositions. Their analysis can be important in connection to health issues and environmental problems. Analytical pyrolysis can be used for obtaining information in all these areas. The technique is also useful for better understanding of the processes occurring during the industrial pyrolysis of polymers with the purpose of recycling.

The present book is a follow-up of a previous one with the title *Analytical Pyrolysis of Natural Organic Polymers* published by Elsevier as vol. 20 in the series "Techniques and Instrumentation in Analytical Chemistry." In addition to the discussion on pyrolysis of various natural polymers, the previous book contains information on chemically modified celluloses, modified starches, etc. For this reason, the present book does not include synthetically modified natural polymers. Information on the pyrolysis process and pyrolytic techniques in general also can be found in the book on natural polymers. These subjects are only summarized here. For the internal consistency of the second book, a few general sections are similar to those in the previous one, although some information is updated.

This book has two main parts, and the material is organized in chapters and sections. The first part of the book has five chapters including an introduction, a discussion on physico-chemistry of thermal degradation of synthetic polymers, a short discussion on instrumentation used in analytical pyrolysis, a chapter discussing what type of information can be obtained from analytical pyrolysis, and a chapter dedicated to the applications of analytical pyrolysis for the analysis and characterization of synthetic polymers. The chapter on applications includes only a few selected examples from the multitude existent in literature, and it is not intended to be exhaustive. Excellent monographs, such as F. W. Billmeyer Jr., *Textbook of Polymer Science*, J. Wiley, New York, 1971; H. H. G. Jellinek, ed., *Aspects of Degradation and Stabilization of Polymers*, Elsevier, Amsterdam, 1980; S. A. Liebman, E. J. Levy, ed. *Pyrolysis and GC in Polymer Analysis*, M. Dekker, New York, 1985; and T. P. Wampler, ed., *Applied Pyrolysis*

Handbook, M. Dekker, New York, 1995, can provide supplementary information regarding these subjects.

The second part is the core of the book. In this part are presented in a systematic manner the main results published in literature regarding the analytical pyrolysis of various classes of synthetic polymers. Some unpublished original results using pyrolysis coupled with gas chromatography/mass spectrometry (Py-GC/MS) also are included in this part. Each polymer class is presented in a different chapter and includes polymers with a particular backbone structure. The polymers with the same backbone but with different side chain groups are discussed in different sections of the same chapter. The main types of polymers discussed in the book include those having in the backbone saturated carbon chains, unsaturated carbon chains, aromatic hydrocarbon groups, ether groups, ester groups, carbonates, anhydrides, sulfides, sulfones, imines, imides, amides, urethanes, ureas, various heterocycles, silicon, phosphorus, etc.

Copolymers are very common synthetic materials, and a significant number of pyrolysis studies reported in literature are dedicated to copolymers. Pyrolysis results for different copolymers are discussed in connection to each homopolymer class. Also, a considerable number of literature references is given in the book for each subject.

The intention of the author was to provide information on pyrolysis for a wide range of readers, including chemists working in the field of synthetic polymers as well as for those applying pyrolysis coupled with specific analytical instrumentation as an analytical tool. Some theoretical background for the understanding of polymer structure using analytical pyrolysis is also discussed. The book is mainly intended to be useful for practical applications of analytical pyrolysis in polymer identification and characterization.

The author expresses his thanks to Mrs. Nancy Qian for assistance with performing the pyrolysis experiments on many synthetic polymers.

Serban C. Moldoveanu

CHAPTER 1

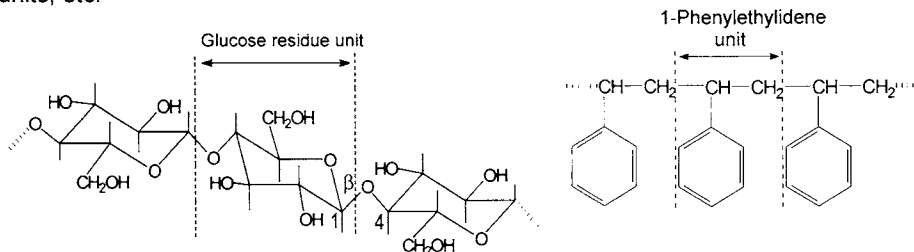
Overview of Organic Synthetic Macromolecules

1.1 INTRODUCTION TO POLYMER CHEMISTRY

- General aspects

Polymer chemistry is an important branch of science, and polymer analysis and characterization is a common subject in scientific literature. Analytical pyrolysis is one of many tools used particularly for polymer identification and for the evaluation of polymer thermal properties. Before a more in-depth discussion on analytical pyrolysis and its application to polymer science, some basic concepts regarding the chemistry of synthetic polymers will be briefly discussed.

A term more general than polymer is that of macromolecule. *Macromolecules* are chemical compounds formed from at least one thousand atoms linked by covalent bonds. They are common as natural substances like cellulose, proteins, lignin, etc., and also as synthetic compounds including plastics, fibers, elastomers, coatings, and adhesives. Many synthetic and some natural macromolecules have repetitive structures and are known as *polymers*. For example, cellulose is made from β -D-glucose residues interconnected by β -glucoside (1 \rightarrow 4) links, polystyrene is made from 1-phenylethylidene units, etc.



The polymers formed from identical repeating units are sometimes called homopolymers, and the name "polymer" is frequently extended to nonrepetitive macromolecules such as various organic geopolymers, lignin, or proteins. The number of repeating units is defined as the *degree of polymerization* (DP). The molecules formed by the union of a few repeating units are known as *oligomers*, and they have a low DP. The molecule that generates the repetitive unit is called a *monomer*. Certain polymers can be formed from the repetition of more than one kind of unit, and they are known as *copolymers*. The repeating units in copolymers may have an ordered repetition or a random one.

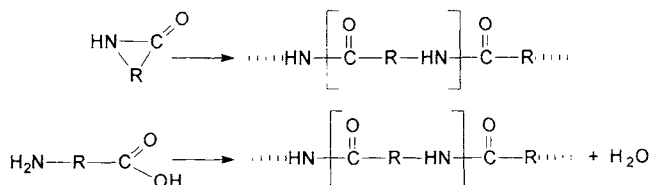
Polymers can be viewed as consisting of a *backbone* on which are attached atoms or groups of atoms. The polymer backbone may have a linear, branched, or network structure. More unusual polymer structures may have peculiar characteristics such as star, comb-like, ladder, or other structures. For linear polymers the backbone extends mainly in one dimension, for sheets in two dimensions, and for reticulate polymers in

three dimensions. However, the coiling of linear polymers or the intermixing of branched structures leads to tridimensional macromolecules.

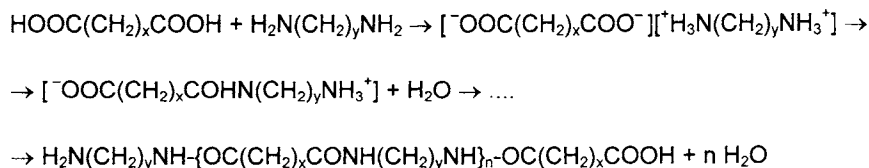
In their molecules, the polymers also contain *end groups*. An end group is the last group in a chain, these not being identical to the repeating units. Depending on the frequency of occurrence of the end groups (related, for example, to the length of polymer chains), the role of the end groups in the property of the polymer can be more or less important. The end groups are counted in the value of the DP.

- Formation of polymers

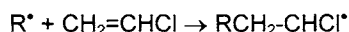
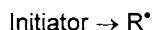
The formation of polymers from the monomers is known as *polymerization reaction*. When more than one basic unit forms the polymer, the process is also named *copolymerization*. The polymerization reactions can be classified into two main groups, *addition polymerizations* and *condensation polymerizations* (or polycondensations). For the addition polymerizations, the resulting polymer has the repeating unit with the same molecular formula as the monomer, and the molecular mass of the polymer is the sum of the molecular masses of all the monomer molecules. For the condensation polymerizations, the resulting polymer has the repeating unit with fewer atoms than that of the monomer or monomers, and the molecular mass of the polymer is less than the sum of molecular masses of the original monomer unit or units because small molecules are eliminated following this reaction. This classification is not adequate for the characterization of the polymer itself, because the same polymer can be formed by more than one type of reaction. For example, a polyamide can be formed by addition from a lactam or by condensation from an ω -aminocarboxylic acid as shown below:



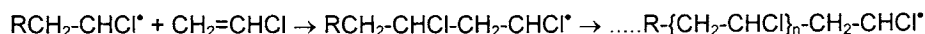
The reactions with formation of polymers also are classified based on another difference in their mechanism. This classification distinguishes *step reactions* and *chain reactions*. In step reactions the polymers are built from the monomer by random individual reactions to form dimers, trimers, tetramers, etc., each resulting molecule being able to participate in a subsequent reaction with a monomer or with an oligomer molecule. This type of reaction may start with molecules having two reactive functional groups in one molecule such as an ω -aminocarboxylic acid. Another possibility consists of reactions between two different types of bifunctional molecules such as a diamine and a dicarboxylic acid as shown below:



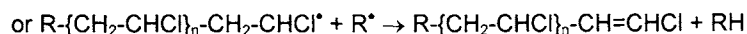
In chain reactions the polymer is formed by successive linking of monomer molecules to the end of a growing polymer chain. These reactions typically have an initiation, a propagation, and a termination stage. The initiation can be caused using a specific compound that generates free radicals (R^{\bullet}), these reacting with the monomer as shown below for vinyl chloride:



Further, the polymerization takes place by a radicalic mechanism, this stage being known as propagation:



The reaction is terminated either by radical coupling or by disproportionation:

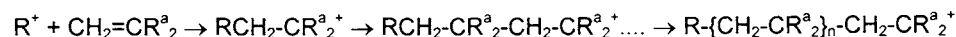


Among the most common free radical initiators are benzoyl peroxide, *tert*-butyl hydroxyperoxide, *tert*-butyl peroxide, dicumyl peroxide, 2,2'-azobisisobutyronitrile (AIBN), potassium persulfate, etc.

A similar role to that of the free radical can be played in certain polymerizations by an ion. For example, cations can be generated from mineral acids or Lewis acids in the reaction with compounds such as water or alkyl chlorides, as follows:

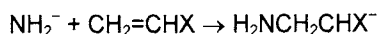


The resulting cation reacts with the monomer in a chain reaction:



For obtaining a cationic polymerization, the new carbocation generated between R^+ and the monomer should have enough stability to be relatively easily formed and to continue the polymerization (for example, $\text{CH}_2=\text{CH}_2$ is not polymerized using a cationic initiator, while $(\text{CH}_3)_2\text{C}=\text{CH}_2$ can be polymerized because the species $\text{RCH}_2\text{-C}(\text{CH}_3)_2^+$ is stable enough to be formed). The stability of the carbocation increases as the chain length increases. Chain transfer reactions are common in carbocation polymerization. The termination reactions typically occur because of the combination of the cationic component with a counterion.

Anions can be used to promote a chain reaction similarly to cations, except that they act as nucleophiles in their reaction with the organic monomer. The anions are frequently formed in a reaction with alkali metals such as Na, K, or Li. As an example, potassium in liquid ammonia forms KNH_2 , which generates NH_2^- anions. These anions further react with the organic monomers in a reaction as shown below:



$$\text{Na}^{\bullet} + \text{CH}_2=\text{CHR} \rightarrow \text{CH}_2\text{-CHR}^{\bullet-} \text{Na}^+ \rightarrow \text{Na}^+ \text{ } ^-\text{CHR-CH}_2\text{-CH}_2\text{-CHR}^- \text{Na}^+$$

Termination reactions of this type of polymerization usually involve an ion transfer. Since the ion transfer requires the presence of a molecular species to which the transfer can occur, it is possible by conducting the reaction with very pure compounds to eliminate the termination step. By unterminated polymerization the final material can remain active indefinitely and is known as a living polymer.

The reaction scheme illustrates the formation of a zirconium complex. It begins with a zirconium tetrachloride molecule (ZrCl₄) and an alkene (R^a-C(R^b)=CH₂). The reaction proceeds through a series of steps, involving the coordination of the alkene to the zirconium center, followed by the formation of a zirconium-alkyl complex. The final product is a complex where the zirconium atom is coordinated to a chlorine atom and a zirconium atom is coordinated to a chlorine atom and a zirconium atom is coordinated to a chlorine atom.

Similarly to other chain reactions, the termination takes place by transfer reactions, internal hydride transfer, etc.

A special type of polymerization is that of cyclic compounds such as lactones, lactams, cyclic ethers, cyclic anhydrides, or cyclic N-carboxyanhydrides that can be polymerized by ionic mechanisms. These compounds can undergo an addition reaction with characters of both chain and step polymerization.

Although a large number of step-reactions are condensations and a large number of radical chain reactions are additions, there are also numerous exceptions. Including both classifications, a more detailed one distinguishes four groups. These groups are (a) polycondensation (step-polymerization with small molecules eliminated following this reaction), (b) polyaddition (step-polyaddition), (c) chain polymerization (chain-polyaddition), and (d) condensative chain polymerization (chain-polymerization with small molecules eliminated following the reaction).

Different reaction mechanisms, although leading to a polymer with identical repeating units, may have a significant impact on the physical properties of the polymer. The polymers may differ in (average) molecular weight, end groups, stereochemistry, chain branching, etc. [1].

- **Formation of copolymers**

When a mixture of two (or more) types of monomers is used as starting material in a polymerization reaction, the result can be the formation of a copolymer. However, different monomers differ significantly in their tendency to enter into copolymers. Even some monomers that are very difficult to polymerize alone or do not form polymers at all may participate very easily in the formation of some copolymers. One such example is maleic anhydride that gives easily copolymers with styrene or with vinyl chloride and forms very difficultly a homopolymer.

In their structure the copolymers may contain the monomeric units randomly, and their overall composition is determined by the composition of the initial feed mixture of monomers (see Section 2.3). Alternating copolymers (*alt*-copolymers) also are known, where the monomers alternate regularly along the chain. Other types include *block* polymers where a linear arrangement of groups of one type of monomers is present, *graft* polymers that have side chain blocks connected to a polymer main chain, *per*-copolymers where ordered sequences of more than two units are present, etc.

The synthesis of different types of copolymers is done following particular procedures depending on the nature of the copolymer. For free radical polymerization, the outcome of the copolymerization depends very much on the nature of the monomers, while in step polymerization it is more common to generate random polymers since the reactivity of the functional groups is less influenced by the length of the molecule to which the groups are attached. Special types of copolymers such as block copolymers can be obtained, for example, by using unteminated anionic polymerization for one monomer, followed by the addition to the living polymer of a second monomer that will continue the polymerization process. The structure of copolymer can be further complicated. For example, block copolymers may have a diblock structure, where the copolymer is made

from two chemically distinct polymer blocks, or a structure where only one of the monomers forms uninterrupted blocks. The blocks can be in a predominantly linear structure, or they can be part of a radial (star) type structure.

Copolymers have a very large range of applications in practice since they may possess properties difficult to attain in homopolymers. For this reason, many polymer samples from common sources are copolymers.

- Polymerization conditions

A large number of experimental conditions to obtain polymers have been developed. The polymerization can be done in homogeneous systems including bulk polymerization and solution polymerization, or heterogeneous system polymerization including suspension and emulsion polymerization. Bulk polymerization of pure monomers may appear as the simplest procedure for polymer formation, but this type of procedure is limited to reactions that are only mildly exothermic. Solution polymerization can avoid overheating, but the final removal of a solvent from the polymer is often difficult. Polymerization in suspension is usually done in water with the monomer as a dispersed phase and the polymer resulting as a suspension. The procedure usually applies stabilizers and agitation of the solution to maintain the dispersion of the monomer. The initiator is typically dissolved in the monomer phase. In emulsion polymerization, the monomer forms a true emulsion in water where also the initiator is present. Detergents are used as emulsion stabilizers and may play an active role in the progress of the polymerization reaction (see e.g. [2]). Other polymerization procedures are known such as solid phase polymerization, inverse phase emulsion polymerization, etc. The subject of polymerization conditions is covered by an enormous body of literature.

- The degree of polymerization and molecular mass distribution

Polymeric materials are typically obtained with a range of DP values. For this reason the characterization of polymers is done using an *average degree of polymerization*. For a polymerization reaction starting with N_0 molecules of monomer, at a certain point during the reaction, the number of molecules is reduced to N . The average degree of polymerization is defined as follows:

$$DP = \frac{N_0}{N} \quad (1.1.1)$$

An average molecular mass (weight) of the polymer also needs to be defined, since components of various molecular masses (weights) M_i are present in the polymer. The number of moles of species "i" in the polymer can be obtained from the typical formula $n_i = w_i / M_i$ where w_i is the weight fraction of the component "i", and M_i is the molecular mass of species "i". The masses of molecules or groups can be calculated using two different conventions. One convention considers the natural isotopic abundance of elements and takes their sum based on the compound chemical formula. For the masses of polymers, the first convention is typically used. The other convention considers only the masses of the most abundant isotope, which is useful for MS

interpretations (as in the case of pyrolysis GC/MS of polymers). For this latter case, the resulting mass is rounded to the unit [3].

The *number-average molecular mass* M_n expressed in g/mol is given by the formula:

$$M_n = \sum x_i M_i = \frac{\sum n_i M_i}{\sum n_i} = \frac{\sum w_i}{\sum w_i / M_i} = \frac{W}{n} \quad (1.1.2)$$

where W is the total weight and the summation is done over all "i" values, and the mole fraction is given by $x_i = n_i / n$ where n is the total number of moles of polymer.

A *weight-average molecular mass* M_w also is used for polymer characterization. This parameter is given multiplying the weight fraction w_i/W by the molecular mass M_i and is defined by the formula:

$$M_w = \frac{\sum w_i M_i}{W} = \frac{\sum w_i M_i}{\sum w_i} = \frac{\sum n_i M_i^2}{\sum n_i M_i} \quad (1.1.3)$$

For an ideal polymer with all molecules having the same molecular mass, $M_n = M_w$, and the polymer is known as a monodisperse system. In most synthetic polymers, $M_w > M_n$, and the ratio $Q = M_w / M_n$ is called *polydispersity index*. The molecular mass (weight) for small molecules is noted MW and does not represent an average.

References 1.1

1. M. P. Stevens, *Polymer Chemistry, An Introduction*, Oxford Univ. Press, New York, 1999.
2. F. W. Billmeyer Jr., *Textbook of Polymer Science*, J. Wiley, New York, 1971.
3. F. W. McLafferty, *Interpretation of Mass Spectra*, University Science Books, Mill Valley, 1980.

1.2 NOMENCLATURE OF POLYMERS

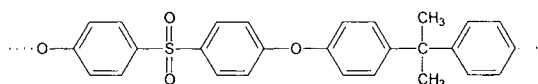
- General aspects

Polymers are typically complex molecules and in some cases not sufficiently characterized regarding their structure. Even the polymers with a simple model structure are always mixtures of macromolecules of different molecular masses (weights). For these reasons a name of the polymer describing the structure with the same exactness as for small molecules is not possible. Besides the commercial names of the polymers, two different scientific systems for naming are in use. The first is a source-based nomenclature and the other is a structure-based one. The source-based nomenclature uses the name of the monomer or of the starting reactant for naming the polymer. For homopolymers that are derived from only one species of monomer, the name of the polymer can be formed by attaching the prefix "poly" to the name of the monomer or of the starting reactant (parentheses are used when the name of the monomer has two or more words). Examples are polyacrylonitrile, polyethylene, polystyrene, poly(vinyl chloride), etc.

The name based on starting reactants is also applied for some condensation polymers such as poly(ethylene terephthalate) or phenol-formaldehyde resin.

The structure-based nomenclature is rather straightforward for linear single strand polymers, which are named "poly(constitutional repeating unit)" [1,2]. The name of the repeating unit is based on the IUPAC nomenclature of bivalent organic groups. For repeating units containing a sequence of subunits, a seniority order from left to right must be followed. This seniority decreases in the following order: heterocycles > heteroatomic groups > carbocycles > acyclic carbon groups. Within each structural type, further seniority is established. For example, for heteroatomic groups the seniority decreases in the order O > S > N > P > Si, etc. For carbocycles a larger number of cycles is senior to a lower number, and a larger cycle is senior to a smaller one. For acyclic carbon groups the seniority is based on the number of C, and for equal number by the number of substituents. In all cases, the seniority is applied only for the polymer backbone.

As an example, the polymer with the structure:



is named poly(oxy-1,4-phenylene-sulfonyl-1,4-phenylene-oxy-1,4-phenylene-isopropylidene-1,4-phenylene).

Specific rules also are applied for polymers with other regular structures such as ladder type polymers or spiro polymers [3]. For single-strand linear copolymers with irregular structures, the name is given as "poly(first constitutional repeating unit/second constitutional repeating unit)", etc. Detailed explanations for polymer nomenclature can be found in various reference materials (see e.g. [4]).

Although there are clear IUPAC rules for naming the polymers, in practice various names for the same polymer are frequently encountered. As an example, a simple polymer such as nylon 6 (commercial name) can be named poly(ϵ -caprolactam), poly[imino(1-oxo-1,6-hexandiyl)], poly(6-aminoheptanoic acid), polycaproamide or poly(pentamethylenecarbonamide).

Besides scientific names, many polymers are indicated by their common name, trade name, brand name, or abbreviation (commercial names) [4]. Typical examples of common names are nylon or silicone. Several nylons are known and the name nylon 6 is used for poly[imino(1-oxo-1,6-hexandiyl)], the name nylon 66 is used for poly(iminohexa-methyleneiminoadipoyl), etc. Trade names such as Teflon[®] for poly(tetrafluoro-ethylene) made by DuPont, Nomex[®] for poly(iminoisophthaloylimino-1,3-phenylene), or Kevlar[®] for poly(iminoisophthaloylimino-1,4-phenylene) are also common. Many abbreviations are in use for both homopolymers and copolymers. Table 1.2.1 gives some of the common abbreviations for polymers.

TABLE 1.2.1. Common abbreviations for polymers.

Abbreviation	Polymer	Abbreviation	Polymer
ABS	poly(acrylonitrile-co-butadiene-co-styrene)	PET	poly(ethylene terephthalate)
ASA	poly(acrylic acid-co-styrene-co-acrylonitrile)	PF	phenol-formaldehyde resin
EP	epoxy	PMMA	poly(methyl methacrylate)
HIPS	high-impact polystyrene or poly(butadiene-co-styrene)	PP	polypropylene
LDPE	low density polyethylene	PPO	poly(phenylene oxide)
MF	melamine-formaldehyde resin	PS	polystyrene
PAA	poly(acrylic acid)	PTFE	polytetrafluoroethylene
PAN	polyacrylonitrile	PU	polyurethane
SBR	poly(styrene-co-butadiene)	PVA	poly(vinyl alcohol)
PBT	poly(butylene terephthalate)	PVAc	poly(vinyl acetate)
PC	polycarbonate	PVC	poly(vinyl chloride)
PE	polyethylene	SAN	styrene-acrylonitrile copolymer

One more way to identify a specific polymer is that using CAS (Chemical Abstracts Service) registry number (CAS#). These numbers are unique identifiers for chemical substances (including polymers), but they have no chemical significance. Depending on the form of the polymer, the same compound may have more than one CAS registry number. CAS registry numbers can be used to provide a link between various nomenclature terms used to describe the polymers.

For copolymers, the name “poly” is also attached to the names of the monomers or starting reactants. For linear macromolecules, between the monomer names an infix is placed indicating, if possible, the type of sequence arrangement. The connective infixes used in polymer names are *-co-* for unspecified structure, *-stat-* for structure obeying a known statistical law, *-ran-* for Bernoullian distribution, *-alt-* for alternating monomeric units, *-per-* for ordered sequence of more than two units, *-block-* for linear arrangement of blocks of one type of monomers, *-graft-* for side chain blocks connected to the polymer main chain, etc. Examples are polystyrene-co-polydivinylbenzene, polystyrene-*block*-polybutadiene, poly[(ethylene glycol)-*alt*-(terephthalic acid)], etc. The prefix copoly with the name of the two monomers separated by “/” or “-” also can be used as a name. Examples are copoly(styrene/divinylbenzene), copoly(styrene/methyl methacrylate), etc. The infix indicating the type of sequence arrangement can be used as a prefix before the word copoly, such as in *block-copoly*(butadiene-styrene) [6].

Macromolecules with nonlinear structure form a special group that includes *branched*, *graft*, *comb*, *star*, *cyclic* and *network* type macromolecules. Also, macromolecular assemblies are known, such as polymer blends, interpenetrating polymers, polymer networks, polymer-polymer complexes. The names of these types of macromolecules can be made using qualifiers such as *-branch-*, *-blend-*, *-i-* indicating crosslinked, etc.

References 1.2

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3. IUPAC, "Source Based Nomenclature for Non-Linear Macromolecules and Macromolecular Assemblies," *Pure Appl. Chem.*, 69 (1997) 2511.
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1.3 MORPHOLOGY OF POLYMERS

- General aspects

From the physical point of view, polymers can be either liquids or solids. However, the distinct differences between the two physical states as they are known for small molecules are not necessarily present for polymers. For example, polymers have two common forms, namely *amorphous* and *crystalline*, the amorphous ones resembling glass. One more separate solid type can be considered crosslinked polymers. In crosslinked polymers, there are tridimensional connections between different parts of the molecule, and the concept of ordered molecules (as in crystals) or disordered molecules (as in amorphous solids) loses its meaning. Even true "crystalline polymers" do not contain 100% crystallized form, and, more properly, they should be indicated as *semicrystalline*. The amorphous form is characteristic to most solid polymers at temperatures above their melting point. Both amorphous and crystalline forms are known for some polymers. Specific macromolecules can be found in liquid crystal form in addition to true liquids.

In amorphous state, solid polymers retain the disorder characteristic for liquids, except that the molecular movement in amorphous solid state is restrained. The movement of one molecule versus the other is absent, and some typical liquid properties such as flow are absent. At low stress, polymers display *elastic properties*, reverting to a certain extent to the initial shape in a relaxation process. However, they can be irreversibly deformed upon application of appropriate force. The deformation and flow of polymers is very important for practical purposes and is studied by a branch of science known as rheology (see e.g. [1]). The combination of mechanical force and increased temperature are commonly applied for polymer molding for their practical applications. The polymers that can be made to soften and take a desired shape by the application of heat and pressure are known as *thermoplasts*, and most linear polymers have thermoplastic properties.

When an amorphous polymer is heated, it passes through a stage where it acquires rubber-like characteristics. The temperature at which this change takes place is known as *glass transition temperature* T_g . The value of glass transition temperature T_g can be measured by different procedures, although some variability in the reported values is seen in literature [2]. A whole group of polymers known as *elastomers* have their glass transition temperature below the ambient. Glass transition temperature is a very important characteristic for polymers because it is significant in numerous practical applications and in polymer processing. At glass transition temperature, most intermolecular interactions that limit the vibration and rotation of molecules as well as some of longer-range molecular motions become negligible. This process also is

associated with an increase in the space between the atoms, i.e. an increase in the free volume. It can be inferred that a compound with small molecules would melt at T_g . However, at T_g , the free movement of macromolecules one versus the other is still not possible and the material preserves its shape. Melting overcomes the last resistance to the molecular movement, but the melting of amorphous polymers does not occur at a precise value and typically takes place within a rather broad temperature interval.

The glass transition temperature is dependent on the structure of the polymer, and for the same polymer varies as a function of the polymer molecular weight. The increase in the molecular weight of the polymer is associated, as expected, with an increase in the

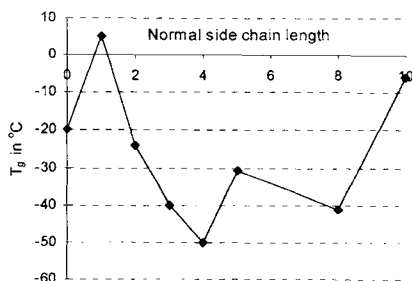


FIGURE 1.3.1. Variation of T_g with the length of the normal side chain for several vinyl polymers.

T_g value. Other effects can be seen, for example, when the polymers have the same backbone structure and attached groups of about the same volume but with different polarity. This increase shows an increase in the T_g , such as for the series polypropylene ($T_g = 5^{\circ}\text{C}$), poly(vinyl chloride) ($T_g = 81^{\circ}\text{C}$), poly(vinyl alcohol) ($T_g = 85^{\circ}\text{C}$). On the other hand, for the polymers with the same backbone and with attached groups of different sizes, there is no straightforward dependence between the group size and the T_g . This aspect is explained by the difference in the packing of the polymer molecules when the side groups vary significantly. Also, the

increased branching in the side chain increases T_g . Groups that restrict free rotation of the polymer molecule have the effect of increasing T_g .

Some polymers that have very high repetitiveness in their molecules may exist in crystalline (semicrystalline) form. This crystallinity is different from that of small

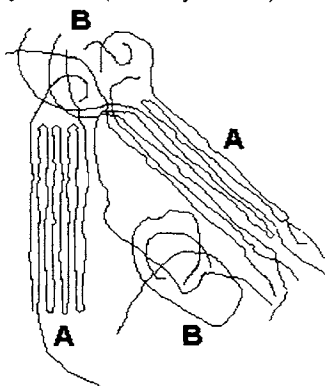
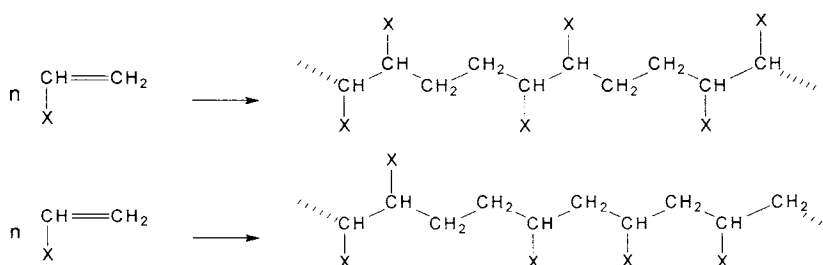


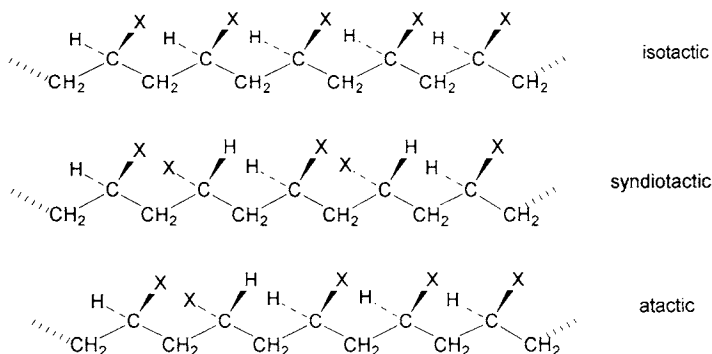
FIGURE 1.3.2. Schematic (two dimensions) representation of crystallites (A) surrounded by amorphous regions (B)

molecules where the molecules are orderly arranged in a crystal. In crystalline polymers, regions of ordered chains exist in the macromolecular matrix. Such ordered regions are called *crystallites*. The individual crystallites are usually interconnected by amorphous regions, as shown in Figure 1.3.2. In crystallites the molecular chains are aligned thermodynamically favorable, and for polymers that have the right structure the crystalline form can be obtained by cooling a polymer melt or evaporating a polymer solution similarly to the generation of small molecule crystals. In addition, crystalline regions can be generated in some polymers by stretching of a polymer sample that aligns the polymer backbone into crystallites. Some crystallites are formed from the same long molecular chain that bends back after a linear portion (crystallite A in Figure 1.3.2)



In practice, the polymerization takes place mainly head-to-tail, and the proportion of other isomers is minor. Structural isomeric polymers may be obtained using different preparation reactions although starting with the same monomers.

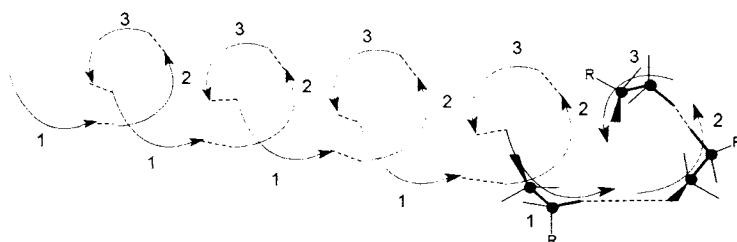
Stereoisomerism refers to molecular species that have the same composition and bond sequence but a different arrangement in space of their atoms. Stereoisomers that are characterized by different interatomic distances between certain atoms that are not bound directly are called *diastereoisomers*. Examples of diastereoisomers are *cis-trans* isomers of compounds containing C = C bonds and *syn-anti* isomers of compounds containing C = N bonds. Other diastereoisomers are not based on the presence of a double bond. For example, a molecule with more than one tetrahedral carbon that has different substituents may form diastereoisomers. For example, for a head-to-tail polymerized monosubstituted vinyl monomer, there are three possible structures indicated as isotactic, syndiotactic and atactic, which are schematically shown below:



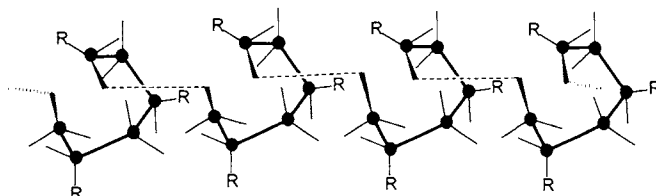
These three forms of the polymer are diastereoisomers, and the property is maintained for the polymer fragments with enough monomeric units. When the polymer is decomposed by thermal degradation, the fragment molecules with four or more monomer units from an isotactic polymer compared to the fragments from a syndiotactic one or an atactic one will be diastereoisomers. These smaller diastereoisomer molecules can be identified after separation on common chromatographic columns [3].

The true conformation in the crystalline structure of a polymer is more complicated, the backbone chain often taking a helical shape in which alternate chain bonds take *trans* and *gauche* positions, such that the carbon chain is not in a plane. For example,

polypropylene, polystyrene, poly(vinyl methyl ether), and other vinyl polymers in isotactic forms have a helical shape with three vinyl units per turn, in a structure as shown below:



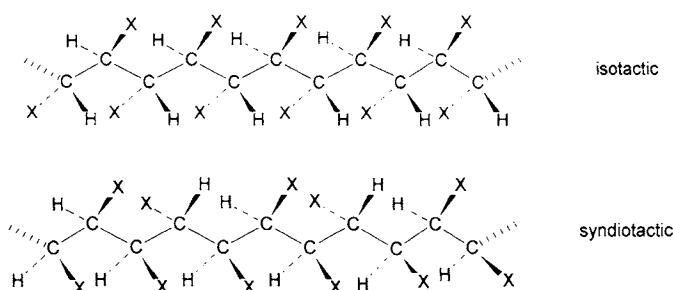
Helical structure with three units per turn



Helical structure of the backbone showing the vinyl units
(the distances between carbons in the backbone are equal)

Other vinyl polymers with larger substituents such as 3-methylpropyl or 2-methylphenyl also have a helical backbone with a larger number of vinyl units per turn, e.g. four or six.

Isotactic and syndiotactic polymers are indicated as stereoregular. Isotactic polymers are typically obtained using insoluble coordination catalysts. Syndiotactic polypropylene has been obtained using homogeneous coordination type catalysts. Disubstituted vinyl polymers obtained from monomers of the form $\text{CH}_2=\text{CX}_2$ do not generate stereoregular polymers, but those obtained from $\text{CHX}=\text{CHX}$ monomer can generate two types of stereoregular materials as schematically shown below:



Stereoregular polymers can be generated from other monomer types such as $\text{X}^a\text{CH}=\text{CHX}^b$, which forms two types of isotactic and one syndiotactic polymer, or from dienes of the type $\text{X}^a\text{CH}=\text{CH}-\text{CH}=\text{CHX}^b$.

The polymer stereochemistry plays an important role in the physical properties of the polymer. As an example, the glass transition temperature for poly(methyl methacrylate)

is $T_g = 105^\circ \text{C}$ for the syndiotactic form, about the same for the atactic form, and $T_g = 38^\circ \text{C}$ for the isotactic form. For this reason, among other analyses performed on polymers, the determination of steric structure is sometimes required.

The polymers from other classes of compounds not necessarily having a carbon chain backbone may have different molecular steric arrangements. The steric arrangement of polyamides, for example, is very important for the capability of forming fibers and for the fiber characteristics (see e.g. Section 13.3).

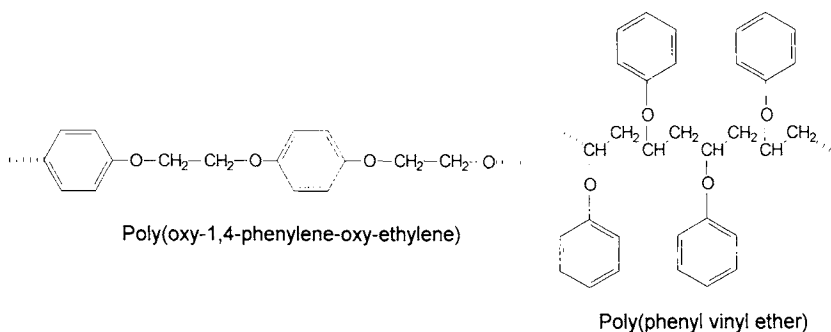
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1.4 MAIN CHEMICAL TYPES OF SYNTHETIC POLYMERS

- Main chemical types of homopolymers

Similarly to small molecules, polymers can be classified based on their chemical nature, i.e. based on the functional groups present in their molecule. However, different from small molecules, one important element in polymer classification is the chemical structure of the polymeric backbone. The attached side atoms or groups of atoms to the polymer backbone play a different role compared to that of the presence of various atom types or groups of atoms in the backbone. For example, it is a significant difference between poly(oxy-1,4-phenylene-oxy-ethylene) that contains phenyl groups and oxygen atoms in the polymer backbone and poly(phenyl vinyl ether) that is a vinyl type polymer with a carbon chain as backbone, although both polymers are ethers. The two polymers are synthesized differently and have quite different properties. Their structures are shown below:



The classification of polymers from the point of view of their chemical nature considers first the chemical structure of the molecular backbone. The chemical nature of the side groups is used only as a second criterion of classification. In some cases, the position of the side groups is well known. In other cases, polymers for practical use may be

obtained by reactions that are not regioselective, and more than one structural isomer can be generated.

Since the molecular backbone can be linear, branched, or network type, this aspect is also important for polymer structure. It is known that most polymers with a linear backbone are thermoplastics, while those with network backbone are thermosetting polymers. However, for classification from a chemical point of view, this differentiation is less significant. Many polymers with linear backbone are obtained from bifunctional monomers (e.g. terephthalic acid and glycol). If the polymer is obtained from similar monomers but with more than two functionalities (e.g. terephthalic acid and ethylene glycerin), the polymer will have thermosetting characteristics. For this reason, this feature is not necessarily used for a classification from the chemical point of view. Based on the chemical structure of the backbone, a number of classes of polymers can be distinguished, as discussed below.

-Polymers with saturated carbon chain backbone include polyolefins, polystyrenes, halogenated polyolefins, halogenated polystyrenes, polyvinyls substituted with various groups such as -OH, -OR, -O(O)C-R, -C(O)O-R, -C(O)-R, -C₅H₄N, etc. In this class also are included polyacrylates, polymethacrylates, polymers with ketone groups in the backbone, as well as other polymers with saturated carbon chain backbone. The polymers with a saturated carbon chain backbone form the most important and common class of polymers.

-Polymers with unsaturated carbon chain backbone form another important class of macromolecules, many of the compounds from this class having properties of elastomers. The most common polymers from this class are obtained from 1,3-butadiene, 2-methyl-1,3-butadiene (isoprene) and their derivatives. Natural rubber, which is poly(*cis*-isoprene), as well as the natural polymers gutta-percha and balata also have an unsaturated carbon chain backbone. For many practical applications, the polymers from this class are subject to a process known as vulcanization, which consists of a reaction with sulfur or S₂Cl₂, and leads to the formation of bridges between the molecular chains of the polymer. This process significantly improves certain physical properties of practical interest. A separate subclass of polymers with unsaturated carbon chain backbone is formed by polyacetylene.

- Polymers with aromatic hydrocarbon backbone include polymers containing in their chain aromatic hydrocarbon rings, or alternating aromatic rings and aliphatic carbon groups. Thermosetting phenolic resins can be included in this class.

- Polymers containing ether groups in the backbone include two subclasses, namely true polyethers and polyacetals. Polyethers such as polyethylene glycol [-O-CH₂-CH₂-]_n having higher polarity compared to polyhydrocarbons are used for many practical applications where some hydrophilic character is necessary. Epoxy resins are also polyethers.

- Polymers containing ester groups in the backbone are common, and they are used frequently as fibers and films, mainly when the polymeric chain contains phenylene groups in addition to the -C(O)-O- groups. Polymers with ester groups in the backbone can be generated from a dicarboxylic acid and a diol, or from a hydroxy acid such as lactic acid or glycolic acid.

- *Polycarbonates and polyanhydrides* are grouped together, although polycarbonates contain the functionality $-\text{O}-\text{C}(\text{O})-\text{O}-$ in their backbone, and polyanhydrides contain the functionality $-\text{C}(\text{O})-\text{O}-\text{C}(\text{O})-$. Both types of polymers are common in practice.

- *Polymers containing carbon-sulfur bonds in the backbone* can be grouped in two categories, polysulfides containing the $-\text{S}-$ atom and polysulfones containing the $-\text{S}(\text{O}_2)-$ group. Some polymers have in their structure a chain of sulfur atoms or $-(\text{S})_x-$ groups. If the sulfur atoms are not part of the polymeric backbone, the polymers are not included in this class. For example, in the vulcanization process of the polymers with unsaturated carbon chain backbone, $-\text{S}-\text{S}-$ bonds are introduced in the polymer, but the resulting product is not classified as polymer with C-S bonds in the backbone, although in hard rubber (ebonite), for example, the content of sulfur can be as high as 32%.

- *Polyimines, polyamides, and polyimides* form an important class of polymers that contain nitrogen atoms in the polymeric backbone. The group of polyimines has amino nitrogens connected by single bonds to aliphatic carbon atoms. Assumed to be formed from monomers containing $>\text{C}=\text{N}-$ groups, the compounds are not indicated as polyamines, although they contain secondary or tertiary amino groups. A typical example of a polyimine is poly(ethylene imine) with the structure $[-\text{CH}_2-\text{CH}_2-\text{NH}-]_n$. Some polyimines are known for their dendrimer structure, which is the result of the capability of the nitrogen atom to form three bonds. One typical example of dendrimer is poly(propylene imine).

A number of polymers of significant practical importance are polyamides. The most common group in this class is probably that of nylons. These compounds have a numbering system indicating how many carbon atoms are in the monomeric unit. The nylons designated by a single number are amino acid polymers with the structure $[-\text{NH}-\text{R}-\text{C}(\text{O})-]_n$, while those designated by two numbers are formed from a diamine and a dibasic acid and have the structure $[-\text{NH}-\text{R}-\text{NH}-\text{C}(\text{O})-\text{R}'-\text{C}(\text{O})-]_n$.

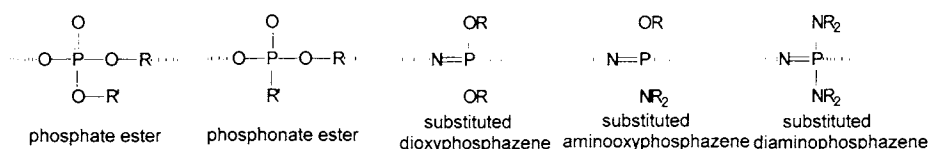
Polyimides are polymers containing the group $-\text{C}(\text{O})-\text{NH}-\text{C}(\text{O})-$ in their structure. Most polyimides have more complicated structures, including oxygen atoms and aromatic rings in their backbone.

- *Polyurethanes and polyureas* are related polymers. Polyurethanes are generated from the reaction of diisocyanates $\text{O}=\text{C}=\text{N}-\text{R}-\text{N}=\text{C}=\text{O}$ with a dihydroxy or polyhydroxy compound, and they contain the group $-\text{NH}-\text{C}(\text{O})-\text{O}-$. Polyurethanes may be considered as esters of carbamic acid or ester amides of carbonic acid. When the polyol is a diol, linear polyurethanes are obtained, and when the polyol has more OH groups, cross-linked polymers are generated. Polyureas are generated from the reaction of diisocyanates $\text{O}=\text{C}=\text{N}-\text{R}-\text{N}=\text{C}=\text{O}$ with a diamine (or polyamine), and they contain the group $-\text{NH}-\text{C}(\text{O})-\text{NH}-$. It is common for polyurethanes and polyureas to incorporate other functional groups into the polymer network, which leads to a variety of materials with a wide range of properties. The hydroxy compounds used in the reaction with the diisocyanate can be polyethers, polyesters, or polyester-polyamides with two or more terminal $-\text{OH}$ groups. Similar to the case for polyurethanes, other polymers with low DP and terminal amino groups can be used to form polyureas. In these cases, the polyurethane or the polyurea can be viewed as a copolymer.

- *Polymers containing heterocycles in the backbone* include a variety of compounds, as the diversity of heterocyclic molecules is quite large. The polymers from this class may contain groups derived from furan, thiophene, pyrrole, isoindole, benzimidazole, benzothiazole, benzoxazole, quinoxaline, etc. Macromolecules with a ladder backbone containing, for example, a phenoxazine unit in their structure also are known. Amino thermosetting resins from melamine can be considered as polymers containing heterocycles in their structure.

- *Polysiloxanes and other silicon containing polymers* form a group of inorganic-organic type polymers with many practical uses. Polysiloxanes, also known as silicones, are the most common polymers in this class. They have a backbone formed from a chain of alternating O and Si atoms in the form $[-O-\overset{\text{Si}}{\underset{|}{\text{---}}}]_n$ and contain organic groups connected to the silicon atom. Common groups are methyl, or phenyl, but silicones with more complicated structures are also known. Other polymers containing silicon atoms may have only C-Si bonds like polysilylenes or may have isolated O-Si bonds.

- *Polymers containing phosphorus in the backbone* are less common in practice. The polymers from this class include organic phosphates, organic phosphonates, and also polymers obtained from substituted phosphazenes such as substituted dioxyiminophosphorane [1], aminoxyiminophosphorane or diaminoiminophosphorane.



The variety of polymers is very large, and special polymers difficult to classify in any of the above groups also are known.

The classification of polymers previously described has been used in this book for the discussion of pyrolysis results. An important class of polymers that is not discussed here is that of chemically modified natural polymers (or semisynthetic polymers). Examples of such polymers are the modified celluloses (carboxymethyl cellulose, ethyl cellulose, etc.), modified starches, casein plastics (Galalith), etc. These types of compounds were discussed in the book on pyrolysis of natural organic polymers [2].

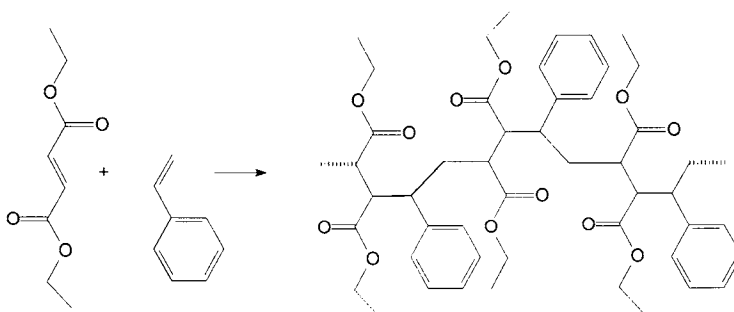
- *The variety of copolymers and the case of alt-copolymers*

The multitude of copolymers is considerable, due to the large number of monomer combinations that can be used in their synthesis. This multitude is further extended by the possibility to obtain from the same comonomers a variety of structures such as random copolymers, *alt*-copolymers, *per*-copolymers, *block*-copolymers, *graft*-copolymers, etc. From the chemical point of view, the copolymers can be generated with monomeric units from the same class or with two or more types of monomeric units. This leads to various backbone structures. Using as a guide the same classification as for homopolymers, it is possible to group the copolymers using the same criteria regarding the backbone composition. However, this would generate numerous

subclasses, which would not be very appropriate for a discussion of the results of copolymer pyrolysis. For this reason, several results on copolymer pyrolysis are presented in this book together with the main classes of homopolymers.

Alt-copolymers have a unique situation among macromolecular compounds. They have an ordered structure of the type $-[A-B]_n$, which can be viewed as the structure of a homopolymer. The fact that *alt*-copolymers can be formed from two starting monomers is not their unique property, and many homopolymers formed in step reactions have an $-[A-B]_n$ formula. For example, Nylon 66, being formed from adipic acid and 1,6-hexanediamine, can be considered an *alt*-copolymer and named poly(hexamethylene-diamine-*alt*-adipic acid), or it can have the name poly(hexamethylene adipamide) or poly(iminohexa-methylene iminoadipoyl) and be viewed as a homopolymer with the structure $-[NH-(CH_2)_6-NHC(O)-(CH_2)_4-C(O)]_n$. Many other examples of the same type can be listed.

Some *alt*-polymers are obtained from radicalic reactions from two monomers mixed together but with the property that each radical reacts almost exclusively with the monomer that is different from the one forming the radicalic end. One such example is that of styrene and diethylfumarate that generate an *alt*-copolymer as follows:



Since there are almost no ideal systems that lead to a perfect *alt*-copolymer in radicalic reactions, these cases can be viewed as true copolymer formation. However, regarding their thermal decomposition, *alt*-copolymers behave similarly to homopolymers.

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1.5 POLYMER BLENDS, COMPOSITE MATERIALS, AND ADDITIVES FOR POLYMERS

- General aspects

It is common in practice to have certain homopolymers or even copolymers mixed together, which modifies some of their characteristics and makes them more suitable for

applications. This can be done by mechanically mixing two or more polymers to form a blend. In a blend, individual macromolecules of the components do not have chemical bonds. However, intermolecular interactions are always present, and physical properties of blends are sometimes quite different from that of individual polymers.

Besides mixtures of polymers or copolymers, a very common procedure to improve desired characteristics of polymers is that of including additives. The additives are typically nonpolymeric molecules. Among the properties that are modified with additives are cost, mechanical properties, color, degradation rate under the influence of light or gases from atmosphere, odor, adhesion to processing equipment, etc. Some polymer properties modified with additives are shown in Table 1.5.1 [1].

TABLE 1.5.1. *Some properties modified with additives in commercial polymers.*

Property modified	Additive type
cost	filler
flexibility	plasticizer
impact strength	impact modifier
strength	filler
slip	lubricants
antistatic property	antistatic agents
bonding between polymer and filler	coupling agents
filler dispersion	wetting agents
moisture dispersion	surfactants, waxes
flammability	flame (fire) retardants
light stability	UV stabilizers
oxidative degradation	antioxidants
color	pigments, dyes
odor	fragrances
light transmission	nucleating agents
melt viscosity	plasticizers
sticking to processing machines	slip agents
shrinkage	shrinkage reducing agents
solution viscosity	thickening agents
heat stability	heat stabilizers
foaming propensity	foaming/defoaming agents
formation of foams	blowing agents
crosslinking	crosslinking agents
rate of curing	promoters

The variety of substances used as additives in polymers is considerable. For example, the fillers may include china clay, various forms of calcium carbonate, talc, silicas (diatomaceous silica), silicates, carbon black, etc. The impact modifiers typically include other polymers. Plasticizers include certain polymers with low M_w (oligomers), dialkyl phthalates, dialkyl sebacates, chlorinated paraffin waxes, liquid paraffinic fractions, oil extracts, etc. Heat stabilizers include heavy metals salts such as basic lead carbonate, basic lead sulfate, dibasic lead phosphite (also acting as a light stabilizer), dibasic lead phthalate, stearates, ricinoleates, palmitates and octanoates of cadmium and barium, epoxide resins and oils, amines, diphenylurea, 2-phenylindole, aminocrotonates. The antioxidants include tris-nonyl phenyl phosphite, 2,6-di-*tert*-butyl-p-cresol (BHT), octadecyl-3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate, etc. The UV stabilizers include modified benzophenones and benzotriazoles. Processing lubricants include calcium stearate, stearic acid, lead stearate, various wax derivatives, glyceryl esters and long-chain acids. Fire retardants include antimony oxide, some pyrophosphates, etc.

Blowing agents include azodicarbonamide, azodiisobutyronitrile, etc. Antistatic agents include quaternary ammonium compounds, etc. With the added complexity due to the presence of these compounds, the analysis of polymeric blends and of practical objects made from polymers containing additives is not always simple.

Composite materials including polymeric components also are frequently encountered in practice. Their use has the aim of achieving specific characteristics for objects of current utility. In a composite material, each component is physically well defined, although sometimes in close contact. Among the common composite materials are the automobile tires that contain a blend of natural and synthetic rubbers reinforced with polymeric fibers (or metallic wire), adhesive tapes that contain an adhesive polymer layered on a stronger non-adhesive sheet of a different polymer, various forms of laminated sheets of two or more different polymers used in floor covering, etc. Although physically separated, the analysis of composite materials is sometimes complicated by the difficulties in taking individual samples from each component.

References 1.5

1. D. W. Van Krevelen, *Properties of Polymers*, Elsevier, Amsterdam, 1990.

1.6 CHARACTERIZATION AND ANALYSIS OF POLYMERS

- General aspects

The concept of polymer properties includes not only the intrinsic material properties, but also the processing properties and the properties of the manufactured objects [1]. All these are of significant practical importance, and a variety of techniques are used for their characterization. The intrinsic properties refer to the polymer as a substance. The processing refers to the fabrication procedures of the manufactured objects.

Processing can play an important role for example in physical properties of polymers, and specific characteristics can be added due to a specific processing. Processing can be done using a variety of techniques such as molding (compression, injection, etc.), blowing, calendaring, casting, coating, extrusion, filament winding, film forming, foaming, forming, laminating, plastisol formation, etc. (see e.g. [2]). The processing needs to be adapted to the polymer intrinsic properties. The article properties are yet another feature of practical importance. These properties include aesthetic properties, resistance to aging, impact strength, dimensional stability, etc. A strong interdependence exists between these three types of properties.

The main type of properties of concern from a chemical point of view are the intrinsic properties. Among these are the mass (molecular weight), the volume, as well as various thermophysical, mechanical, optical, electrical, transport properties, etc. Analytical pyrolysis is able not only to probe some thermophysical properties of polymers, but also to give some structural information that can be used indirectly for other characterizations of polymers.

- Techniques for evaluation of molecular mass and molecular mass distribution

Since a polymer contains components of various molecular masses (weights) M_i , the information on chemical composition of the polymer does not give its molecular mass (number-average molecular mass or weight-average molecular mass). Since the average molecular mass plays an important role for many properties of the polymer, its determination is frequently necessary. Several procedures applied for this purpose are briefly discussed here. One procedure that can be applied for determination of number-average molecular mass is based on the determination of end-groups. By determining the number of milliequivalents of end-groups meq_{eg} in a sample with the weight W , the number-average molecular mass (weight) can be determined by the expression:

$$M_n = \frac{2000 \ W}{\text{meq}_{\text{eg}}} \quad (1.6.1)$$

The determination of the content of end groups can be done using, for example, simple chemical titration for groups such as $-\text{COOH}$, spectrophotometric determination after tagging with specific dyes, radioactivity measurement after tagging with radioactive reagents, etc. The precision of the analysis of end groups should be very good because the concentration of end groups in the polymer is typically low and a small deviation in meq_{eg} gives a large deviation in M_n . Also, the procedure can be applied only to linear polymers, as branching produces errors in this measurement.

Another known procedure for the measurement of number-average molecular mass is based on membrane osmometry. This can be done using van't Hoff equation:

$$(\Pi/c)_{c=0} = RT/M_n + A c \quad (1.6.2)$$

where Π is the osmotic pressure measured with an osmometer, c is the concentration in g/L, R is the gas constant ($R = 8.31451 \text{ J deg}^{-1} \text{ mol}^{-1} = 1.987 \text{ cal deg}^{-1} \text{ mol}^{-1} = 0.082 \text{ L atm deg}^{-1} \text{ mol}^{-1}$), T is temperature in Kelvin deg. K° , and A is a constant. A plot of reduced osmotic pressure Π/c versus the concentration (in g/L) is linear and has the intercept RT/M_n . Impurities consisting of small molecules produce errors in this procedure, but membrane osmometry is still a common way of measurement, and it is applied for M_n values between $5 \cdot 10^4$ to $2 \cdot 10^6$.

Among other techniques used for M_n or M_w measurements are light scattering, mass spectrometry, ultracentrifugation, viscometry, cryoscopy, ebullioscopy, vapor pressure osmometry, etc. Light scattering, for example, allows the determination of weight-average molecular mass M_w through the measurement of turbidity τ of a series of solutions of different concentrations of polymer followed by the extrapolation to zero of the concentration. The values for τ are obtained as the ratio $\log_{10} P_0/P$ where P_0 is the radiant power of the light entering the sample and P that of the light exiting the sample. The value of τ is related to M_w by the expression:

$$\frac{Hc}{\tau} = \frac{1}{M_w P(\theta)} + Ac \quad (1.6.3)$$

where H , and A are constants for a specific polymer, $P(\theta)$ is a function of the angle θ at which τ is measured and $P(0) = 1$, and c is the polymer concentration. The values for A are in general very small.

Cryoscopy and ebullioscopy can be used for the measurement of M_n for polymers in a similar way to the application on smaller molecules, and the procedure is used mainly when $M_n < 2 \cdot 10^4$. MALDI-MS (matrix-assisted laser desorption ionization-mass spectroscopy) allows the measurement of both M_n and M_w , as well as the molecular weight distribution, which indicates the variation of w_i (weight fraction of the component "i"), as a function of M_i .

Molecular weight distribution also can be measured using ultracentrifugation, or more commonly size exclusion chromatography (SEC). Size exclusion chromatography is also known as gel filtration when it is used to separate molecules in aqueous systems, or gel permeation (GPC) when it is used to separate organic polymers in non-aqueous systems. The separation in SEC is similar to that in HPLC, and for a specific polymer it generates a chromatographic peak. A column packed with a porous medium is used for the separation. The separation depends on the hydrodynamic volume or "effective" molecular size of the solute, the smaller molecules being retained longer than the larger molecules. This process is determined by the fact that small molecules can enter freely the pores (interstices) of the gel and are retained longer, while the larger molecules cannot enter the pores and are flushed by the eluent. Numerous materials are currently available for SEC including Sephadex, polyhydroxymethacrylate, polyvinylacetate, various dextrans, porous silica, acrylamide-methylene bisacrylamide, agarose, polymethylmethacrylate, polystyrene, styrene-divinylbenzene copolymer, etc. The solvents used for these phases can be organic organic/aqueous or aqueous [3].

The parameters used for the formal characterization of the separation process in SEC are those used in HPLC. In SEC, the retention volume V_R (in GPC typically called elution volume) is larger for small molecules and much smaller for large molecules. A typical relation between V_R and the molecular weight is given by the expression:

$$V_R = A + B \log (M_i) \quad (1.6.4)$$

Since a range of M_i values are usually present in a polymer, the chromatographic peaks generated in SEC are usually broader than in conventional HPLC. The linearity between

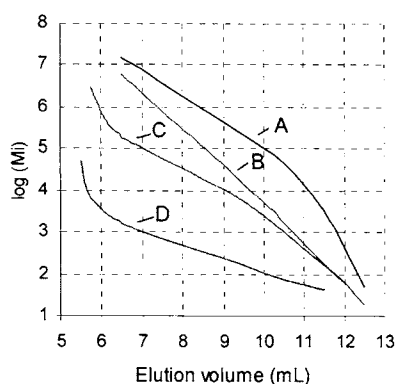


FIGURE 1.6.1. Calibration curves of M_i vs. elution volume in GPC.

$\log M_i$ and the elution volume is utilized for the characterization of molecular weight distribution of the polymer. A wider molecular weight distribution in the polymer generates a wider peak. Expression (1.6.4) is valid only for a certain range of M_i values, and Figure 1.6.1 shows four types of curves common for the calibration in GPC. As seen in Figure 1.6.1, only certain ranges show linearity, the deviation appearing at the end of the calibration interval (curve A), at the beginning of the calibration interval (curve D), or at both ends (curve C). Due to possible deviations from linearity, as shown in Figure 1.6.1, the dependence between M_i and the elution volume is typically calibrated in the molecular range of interest using polymer standards

with known molecular weight. The steric exclusion as a unique mechanism for the separation of polymers is sometimes difficult to achieve because other types of interactions may be present simultaneously with size exclusion. Although no sorption is assumed between the stationary phase and the analytes, this restriction is frequently difficult to achieve. When specific interactions take place between the stationary phase and the solutes, deviations from the expected values of the elution volume may appear.

Comparing the instrumentation used in GPC and that used in conventional HPLC, there are many similarities. Only a few construction details are different for GPC instrumentation, where the control of the column temperature is more important than in other techniques. The gel permeation process is more sensitive to temperature changes than standard sorption HPLC. Constant temperature is necessary for obtaining good reproducibility of the calibration $\log M_i$ vs. V_R . Also, some polymers are soluble in specific solvents only at temperatures above ambient, and an increased temperature during separation is necessary to maintain the solutes in solution.

- Techniques for the analysis of chemical composition and structure of polymers

The characterization of polymer chemical composition is important in numerous practical applications. The polymer identification can be done using various techniques. One of them is the chemical method, which involves reagents that are able to react with the polymer. Oxidation, for example using periodic acid or lead tetraacetate, can be applied to polymers containing 1,2 diol groups, ozonolysis can be applied to polymers containing double bonds, hydrolysis can be applied to esters and amides [4].

More frequently than chemical techniques, the spectroscopic methods of analysis are used for the determination of polymer chemical composition. Among these techniques the use of infrared (IR) absorption spectra as fingerprints for polymer identification is probably the most common. The IR absorption is produced by the transition of the molecules from one vibrational quantum state into another, and most polymers generate characteristic spectra. Large databases containing polymer spectra (typically obtained using Fourier transform infra-red spectroscopy or FTIR) are available, and modern instruments have efficient search routines for polymer identification based on matching an unknown spectrum with those from the library. For specific polymers, the IR spectra can reveal even some subtle composition characteristics such as interactions between polymer molecules in polymeric blends.

Raman spectroscopy, which measures the vibrational satellites generated when the polymer is irradiated with an intense monochromatic light such as a laser, also can be used for polymer identification. Since IR absorption of the polymer is difficult to study in water solutions because of the strong IR absorption of water, Raman spectroscopy is particularly useful for the study of polymer water solutions.

Of considerable importance in the determination of polymer composition and structure is nuclear magnetic resonance (NMR) spectroscopy. A large number of literature reports are available regarding the application of this technique in the study of polymers (see e.g. [5]). This technique allows the identification of various structural units in polymers based on the chemical shift and spin-spin coupling either in proton NMR spectra or ^{13}C

NMR spectra, either in solution or in solid state. Details about polymer structure such as stereochemistry and monomer sequencing can be obtained using this technique [6].

Many other spectroscopic techniques are used for the study of polymers, some having general applicability and others being used for a specific property characterization. For example, UV absorption spectroscopy has been used for the analysis of residual monomers and the presence of antioxidants in a polymer. Electron spin resonance, ESR (or electron paramagnetic resonance, EPR), has been used for the study of free radicals in polymers during the polymerization process or for the measurement of free radical formation upon the irradiation of the polymer with UV light or gamma rays. X-ray diffraction has been used for the determination of spatial arrangement of the atoms in a polymer and for the measurement of the degree of crystallinity.

Other techniques also have been applied for polymer analysis. Among these, mass spectrometric techniques have been used more and more frequently in the analysis of polymers [7]. For example, field desorption (FD) has been used for the analysis of polymers, mainly of hydrocarbon type, with up to $M_w = 10,000$ [8]. Another MS technique used in polymer analysis is secondary ion mass spectrometry (SIMS). Similar to SIMS, except that the sample is bombarded with atoms instead of ions for ionization is fast atom bombardment (FAB), which has been used for the analysis of polymers such as polyglycols [9]. LC/MS techniques, typically with electrospray ionization (ESI), also were used in polymer analysis. ESI generates multiple charged quasimolecular ions, but the mass range for the mass spectrometric detector still needs to be high in order to detect heavy ions. For this reason the technique has been used in connection to Fourier transform ion cyclotron resonance mass spectrometers [10]. One of the most promising mass spectral techniques used in polymer analysis is matrix-assisted laser desorption ionization-mass spectroscopy or MALDI (typically done using a time-of-flight spectrometer and known as MALDI-TOF) [11]. In MALDI the analytes are not directly ionized. Only the matrix made from an aromatic compound containing oxo, hydroxyl, and carboxyl groups is ionized with the laser beam, followed by the charge transfer to the analyte. The technique offers a mild ionization for the macromolecules and an excellent way of polymer analysis. The technique still requires a mass spectrometer with high mass range (TOF, ion cyclotron resonance, etc.). More complex mass spectral techniques also were used in polymer analysis, including several MS/MS techniques [12].

Specific spectroscopic techniques are used for the analysis of polymer surface (or more correctly of a thin layer at the surface of the polymer). They are applied for the study of surface coatings, surface oxidation, surface morphology, etc. These techniques are typically done by irradiating the polymer surface with photons, electrons or ions that penetrate only a thin layer of the polymer surface. This irradiation is followed by the absorption of a part of the incident radiation or by the emission of specific radiation, which is subsequently analyzed providing information about the polymer surface. One of the most common techniques used for the study of polymer surfaces is attenuated total reflectance in IR (ATR), also known as internal reflection spectroscopy. Other techniques include scanning electron microscopy, photoacoustic spectroscopy, electron spectroscopy for chemical analysis (ESCA), Auger electron spectroscopy, secondary ion mass spectroscopy (SIMS), etc.

Another group of techniques used for the study of polymer structure is covered under thermal analysis. Thermal decomposition of polymers in general is a field of considerable interest, the resistance of polymers to heat being of major practical importance. Thermal analysis includes thermogravimetric analysis (TGA), differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermomechanical analysis (TMA), and evolved gas analysis (EGA) [13]. If a physical property of a polymer is measured during heating as a function of temperature, the technique is commonly named a *thermoanalytical* technique. Thermal properties, including glass transition temperature, crystalline melting point, thermal stability, flammability, etc., are measured using dedicated instrumentation. In thermogravimetric analysis (TGA), for example, the weight is continuously measured as a polymer sample is heated in air or in an inert atmosphere. The weight loss occurs initially due to the evaporation of residual volatile compounds in the polymer (water, solvents) and then due to the polymer decomposition and elimination of volatile fragments. This technique allows the determination of the thermal stability of the polymer. The determination of glass transition temperature is typically measured using DTA or DSC. In DTA the polymer sample and an inert reference material, such as alumina, are continuously heated and the temperature of the two materials measured simultaneously. When endothermic or exothermic processes occur in the polymer, its temperature becomes lower or respectively higher than that of the inert material. This allows the detection of glass transition temperature or of other transformations in the polymer. In DSC the sample and the reference are heated separately at constant temperatures while the difference in energy ΔQ required to obtain the same temperature is measured. The plot of the derivative $d\Delta Q/dt$ (where t is time) as a function of temperature T allows the detection of endothermic and exothermic processes similar to DTA. The change in the slope of the graph indicates glass transition, an exothermic process may indicate crystallization or an exothermic reaction, an endothermic process may indicate melting, vaporization, etc. Thermal transitions also can be detected using thermomechanical analysis (TMA). In this technique, a change in volume or in the tensile modulus indicate transformations as a function of increasing temperature.

One technique related to polymer thermal properties is analytical pyrolysis (see e.g. [14]). *Pyrolysis* is the name applied to a chemical transformation induced by thermal energy alone when a compound is heated at a temperature significantly higher than ambient. The main effect of pyrolysis is typically the decomposition of the initial compound with formation of smaller molecules. *Analytical pyrolysis* is a technique used for the characterization of a material (or a chemical process) based on the results of chemical degradation reactions induced by thermal energy [15–17]. Pyrolysis and analysis of pyrolysates (analytical pyrolysis) may be included in the group of thermal analysis techniques. However, this technique is considered somehow apart from the other thermoanalytical techniques such as thermometry, calorimetry, thermogravimetry, differential thermal analysis, etc. In contrast to analytical pyrolysis, thermoanalytical techniques are not usually concerned with the chemical nature of the reaction products during heating. Pyrolysis can be viewed as a special type of thermal decomposition, which allows the study of the formation of products from polymers under heat. Some overlap still exists between analytical pyrolysis and other thermoanalytical techniques. For example, the analysis of thermal decomposition products can be done during other thermoanalytical measurements. This does not transform that particular thermoanalysis into analytical pyrolysis (e.g. [18]). A typical example is the analysis of the gases

evolved during a chemical reaction as a function of temperature, known as EGA (evolved gas analysis).

Pyrolytic reactions usually take place at temperatures higher than 250–300° C, commonly between 500° C and 800° C. The chemical transformations taking place under the influence of heat at a temperature between 100° C and 300° C are called *thermal degradations* [19] and not pyrolysis. Ideally, besides the decomposition produced by heat, no other reactions occur during pyrolysis, but in reality reactions may take place between the products generated in the initial pyrolysis step. Also, the nature of the environment in which pyrolysis takes place should not influence the process. In fact, the ambient atmosphere or various catalyst-like materials present together with the compound to be pyrolyzed may influence pyrolysis. Usually, pyrolysis is performed in an inert gas or at reduced pressure to eliminate the reaction with the ambient atmosphere. However, pyrolysis in the presence of a specific reagent (such as some oxygen) or in the presence of a catalyst added intentionally can be practiced. Pyrolysis in a gas mixture containing oxygen also can give information about polymer flammability, although more specific tests are developed for testing this characteristic [20].

Analytical pyrolysis has significant advantages requiring only a very small amount of sample (typically less than 1 mg [21]), has excellent reproducibility, can be extremely sensitive when the analytical instrument is, for example, a GC/MS system, provides insight on the composition of the analyzed material and also on its thermal properties, etc. The first step in this technique is the pyrolysis reaction. Pyrolysis itself, being a chemical reaction, does not provide analytical data unless it is associated with some kind of measurement process. The measurement is commonly part of a typical analytical technique such as a chromatographic or spectroscopic one. The purpose of the analytical technique is the analysis of the pyrolysis products (*pyrolysate*). One of the most common analytical techniques associated with the pyrolysis process in analytical pyrolysis is gas chromatography, leading to a technique known as *pyrolysis-gas chromatography* (Py-GC). Another common technique is *pyrolysis-gas chromatography/mass spectrometry* (Py-GC/MS). In this technique the volatile pyrolysates are separated and analyzed by on-line gas chromatography/mass spectrometry. Other combinations of pyrolysis/analytical technique also are known, such as *pyrolysis-infrared spectroscopy* (Py-IR). Various types of analytical information can be generated including qualitative, quantitative, or structural (see e.g. [14]).

Because the knowledge of polymer properties is critical for so many practical applications, a significant number of other procedures and tests have been developed solely for the measurement of these properties. Mechanical properties including tensile modulus, elongation, flexural strength, fatigue, impact strength, hardness, abrasion resistance, etc. are typically measured using dedicated instruments. Tensile modulus, for example, is measured by stretching a strip of polymer of known dimensions, applying a specific tensile stress σ , and measuring the tensile strain ϵ in sample length. For a stress $\sigma = F/A$ where F is the force (e.g. in dynes) applied to stretch the polymer sample and A is the cross section area of the sample (e.g. in cm^2), with a resulting strain $\epsilon = \Delta L/L$ where ΔL is the change in the sample length L , the tensile modulus E is defined by:

$$E = \sigma/\epsilon \quad (1.6.5)$$

The tensile modulus E is not a constant when σ varies, and it also depends on temperature T . For these reasons, curves showing the dependence of σ vs. ε at constant temperatures or of E vs. T are used for the understanding of polymer behavior under mechanical stress. The value of E (in dyn cm^{-2} or N m^{-2}) is usually given at polymer break.

The measurement of many other polymer characteristics are of practical importance. Among these are various electrical properties such as volume resistivity, surface resistivity, dielectric constant, arc resistance, etc. Also, solubility properties, polymer-polymer compatibility [22], chemical resistance, resistance to radiations, etc. are measured on polymers (see e.g. [1]).

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CHAPTER 2

*Thermal Decomposition of Polymers***2.1 THE CHEMISTRY OF POLYMER THERMAL DECOMPOSITION****- General aspects**

Thermal decomposition of polymers is a subject of considerable interest for many practical purposes. As shown in Section 1.6, a number of analytical techniques including analytical pyrolysis are used for polymer thermal characterization. The chemical processes occurring when a polymer is heated depend on the heating temperature, heating rate, the atmosphere in which the heating takes place, etc. [1]. Various aspects of thermal decomposition processes of synthetic polymers are thoroughly discussed in various publications (see e.g. [2]). Processes of particular interest in this book are the reactions that occur when the polymer is heated at temperatures between 500° C and 800° C (considered the typical range for pyrolysis). Analytical pyrolysis also implies a fast rate of temperature increase, of the order of 10,000° C/s. The role of temperature in the pyrolysis is further discussed in Section 3.1, and detailed descriptions of pyrolytic reactions for particular polymers are given in Part 2 of this book. Only some general aspects regarding the chemical reactions that take place during pyrolysis are discussed in this section.

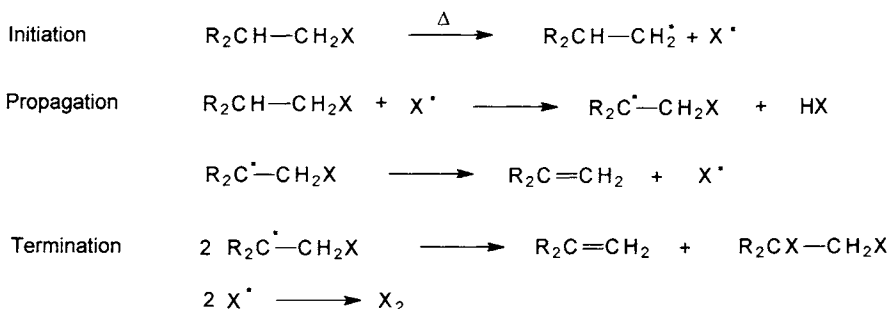
In an ideal case, pyrolysis consists of one decomposition reaction at an elevated temperature. As a result, smaller molecules are generated, being obtained only as fragments of the initial compound. In the majority of cases, pyrolysis of one molecular species consists of several pyrolytic reactions occurring simultaneously or sequentially. The path of a pyrolytic process depends on the experimental conditions, the most important of which is the heating temperature. After a first pyrolytic reaction step, it is common to have subsequent reaction steps. In this case, the initial decomposition step is followed by other pyrolytic reactions of the smaller molecules generated from the initial compound. Therefore, in the case of a polymer, pyrolysis of both small and large molecules occurs. Besides thermal decompositions, the pyrolysis products may react between themselves, generating new compounds. In some cases even formation of complex condensation products may take place, the result being indicated as char. The char may contain molecules larger than the initial polymer. The result is that pyrolysis is typically a complex sequence of chemical reactions generating a variety of compounds.

- Reaction types and mechanisms in pyrolysis

Reactions of several types may take place in pyrolysis (see e.g. [3]), the most common ones being eliminations and rearrangements. Other reactions such as oxidations, reductions, substitutions, or additions also are possible.

In an elimination reaction, fragments of a molecule are removed and form a new molecule. Elimination involving a *free radical mechanism* operates in many pyrolytic reactions. First, an initiation occurs by pyrolytic cleavage, followed by

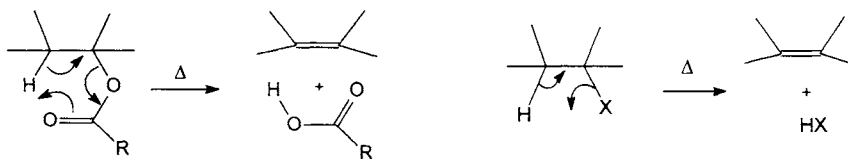
propagation and termination with the result of molecular fragments formation. A schematic example of free radical elimination is shown below (heating is symbolized by Δ):



As further shown, polymer chain scission or side scission of many linear polymers takes place through this mechanism. At higher temperatures (600–900° C) this type of reaction is also common for small molecules, which explains in some cases the formation of unsaturated or aromatic hydrocarbons from larger aliphatic ones.

The free radical formation and propagation process usually occur with the dissociation of the weaker bonds. Besides the weaker bonds, other bonds also can be dissociated, which happens mainly when there are small differences between the bond dissociation energies. The strength of the bond being broken is not always known, and in some cases can be derived from tabulated heats of formation as shown in Section 2.2.

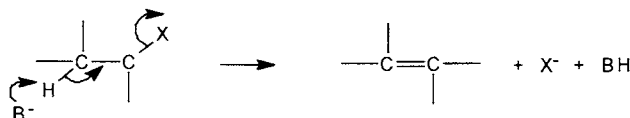
The β -elimination with two groups lost from adjacent atoms is another common reaction in pyrolysis, usually taking place with an E_i mechanism and not involving free radicals. An α -atom is the atom bound to a specific group or bond, and any atom adjacent to it is indicated as a β -atom. β -Eliminations or 1,2-eliminations involve, for example, the elimination of a group from α -atom and a hydrogen from the β -atom. For polymers where the pyrolysis takes place in condensed phase, E_2 and E_1 mechanisms are not excluded. The E_i mechanism involves a cyclic transition state, which may be four-, five- or six-membered [4]. No discrete intermediate is known in this mechanism (concerted mechanism). Two examples of reactions with E_i mechanism involving different sizes of cyclic transition state are shown below [3]:



The two groups (one being the H in the above examples) leave at about the same time and bond to each other. The E_i mechanism is characterized by its kinetics that is of the first order, the lack of free radicals (free radical inhibitors do not slow down the reaction), and that the elimination takes place in a *syn* position. During pyrolytic reactions of E_i

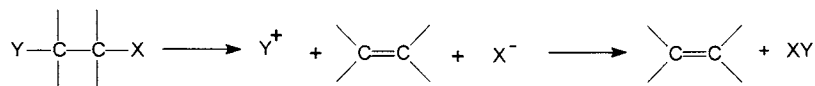
type, if a double bond is present, the formation of a conjugate system is preferred if sterically possible. Otherwise, the orientation in the pyrolytic elimination is statistical and is determined by the number of β hydrogens. The newly formed double bond goes mainly toward the least substituted carbon (Hofmann's rule). In the bridged systems, the double bond is formed away from the bridgehead. Also, for the E_i mechanism, a *cis* β hydrogen is required. Therefore, in cyclic systems, if there is a *cis* hydrogen on only one side, the double bond will go that way. However, when there is a six-membered transition state, this does not necessarily mean that the leaving groups must be *cis* to each other, since such transition states do not need to be completely coplanar. If the leaving group is axial, then the hydrogen must be equatorial and *cis* to the leaving group, since the transition state cannot be realized when the groups are both axial. But if the leaving group is equatorial, it can form a transition state with a β hydrogen that is either axial (*cis*) or equatorial (*trans*).

Besides E_i elimination, in some cases, an E_1 elimination mechanism can be followed, and the more stable olefin is formed. Instead of Hofmann's rule, Zaitsev's rule is obeyed (the double bond goes mainly toward the most highly substituted carbon). In some reactions the direction of elimination is determined by the need to minimize steric interactions, sometimes even when the steric hindrance appears only during the transition state. Also an E_2 mechanism may be followed. It should be remembered that an E_2 reaction requires a proton acceptor and occurs as follows:

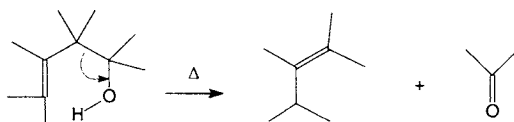


Impurities in the polymer may act as a proton acceptor, or the polymer in itself may act as a base, for example in the elimination of an acid during pyrolysis.

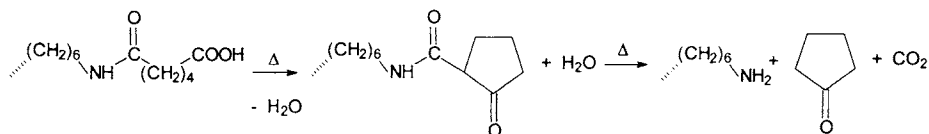
In an elimination, one carbocation can be a leaving group. In this situation, the reaction is called a fragmentation. The reaction commonly takes place in substances of the form $\text{Y}-\text{C}-\text{C}-\text{X}$, where X could be halogen, OH_2^+ , OTs, NR_3^+ , etc. (Ts is p-toluenesulfonate or tosylate). The fragmentation can be written schematically in the form:



The double (or triple) bond formation does not take place exclusively between carbon atoms. It may occur between carbon and nitrogen or carbon and oxygen. An example is the pyrolysis of β -hydroxy olefins:



Besides β eliminations, 1,3 or 1,n eliminations also may take place, for example during pyrolysis with the formation of cycles. One reaction of this type takes place during the pyrolysis of nylon 6,6:

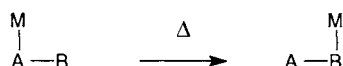


Not only small molecules are eliminated in this type of reaction. Polymer chain scissions also may occur with β -elimination.

The *hydrogen elimination* also can be considered an oxidation and is another common reaction in pyrolysis. The reaction can be favored thermodynamically due to the positive entropy of these reactions (the heat of formation for H_2 is zero).

Another type of reaction in pyrolysis is the *rearrangement*. A rearrangement is a reaction in which a group moves (migrates) from one atom to another in the same molecule. A variety of rearrangements can take place during pyrolysis, such as migration of a group, electrocyclic rearrangements, and sigmatropic rearrangements.

Most migrations take place from one atom to an adjacent one (1,2 shift). However, migrations over higher distances are also known. A typical 1,2 shift takes place as follows:



The migration group M may move with its electron pair, without its electron pair, or with only one electron. In this last case, a free radical rearrangement takes place. The free radical rearrangement involves a first step of free radical formation, and then the actual migration takes place. During pyrolysis, under the influence of heat, the formation of free radicals is common. A typical characteristic for 1,2 free radical migrations is that this type of migration is not known for hydrogens, is uncommon for methyl groups, and is not too frequent for alkyl groups in general. More complicated mechanisms may occur for diradicals. The 1,2 shifts are more common for aryl, vinyl, acetoxy, and halogen migrating groups. Longer free-radical migrations are known for hydrogen.

A different type of known rearrangement is the electrocyclic rearrangement. This takes place for example for 1,3,5 trienes, which are converted to 1,3 cyclohexadienes when heated, as follows:



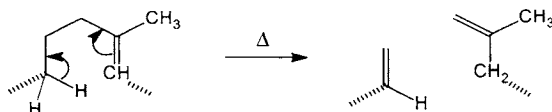
Sigmatropic rearrangements are also non-1,2 shifts. This type of rearrangement consists of a migration of a σ bond adjacent to one or more π systems to a new position in the molecule, with a new reorganized π system.

Oxidations and reductions also may take place during pyrolysis as a subsequent reaction to the initial process. Certain free-radical substitutions that involve the transfer of a hydrogen atom also can be considered oxidation/reduction reactions. It should be noted that oxidation due to the presence of oxygen (intended or accidental) also may take place during pyrolysis (below ignition temperature).

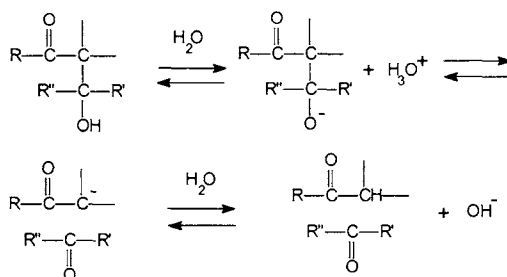
Either as a first step of pyrolysis or as a result of the interaction of molecules from previous pyrolysis steps, substitutions and additions also can take place during the pyrolytic process. The *nucleophilic substitution* takes place with the attack of a reagent that brings an electron pair to the substrate. This pair is used to form a new bond. The leaving group retains its electron pair. Decarboxylation mechanism of aromatic acids is probably an *electrophile substitution*.

Free radical substitutions are very common in pyrolytic reactions. An example of this type is the formation of biphenyl from benzene above 700° C. This reaction can be viewed as an oxidation because of the hydrogen elimination.

Some pyrolytic reactions can be seen as a reverse (retrograde) addition. Diels-Alder reaction for example is known to be reversible, and *retro Diels-Alder reactions* are rather common. The retro-ene reaction (retro hydro-allyl addition) also can take place with the following mechanism:



Retro-aldol condensations also are known to take place during pyrolysis. The mechanism of these reactions can be written as follows:



More paths for the same process is a common occurrence in pyrolysis, and more than one mechanism is frequently needed to explain the variety of reaction products.

- General aspects regarding the chain scission in pyrolysis

Polymer degradation reactions are frequently categorized based on the site in the macromolecule structure where the reaction occurs. This leads to the following classification of scission reactions: a) polymeric chain scission, b) side group reactions, c) combined reactions [5, 3]. These reactions follow one of the mechanisms described previously, but this different classification allows a better correlation of the nature of the reaction products with the structure of the polymer and provides more understanding regarding the expected pyrolysis products.

The polymeric chain scission is an elimination reaction that takes place by breaking the bonds that form the polymeric chain. This reaction may take place as a successive removal of the monomer units (end cleavage) or may occur as a random cleavage of the polymeric chain. The random cleavage takes place mainly when the bonding energies are similar along the chain. The distinction between the two types of scission can be made based on the extent of monomer evolution and on the measurement of the polymer average molecular weight when heating the polymer at a temperature below typical pyrolysis value. The slow evolution of monomer and rapid decrease of the molecular weight is an indication of random cleavage.

Many chain scissions reactions have a free radical mechanism [6, 7]. As previously indicated, these reactions will be characterized by an initiation step, a propagation and a termination.

- Initiation reactions during the chain scission in pyrolysis

Initiation consists of the formation of free radicals under the influence of heat. These radicals may consist of two long chain free radicals or of one free radical chain plus one monomeric free radical when the reaction takes place at the end of the polymeric chain. Therefore, two main types of scission can be distinguished: *random scission* and *end chain scission*. Using the notation P_n for a polymer with $DP = n$, and R_n for a polymeric radical with $DP = n$, the end scission can be written schematically as follows:



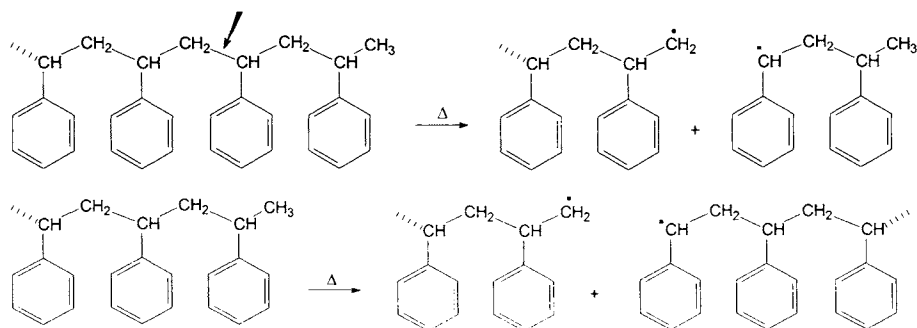
while the random scission can be written in the form:



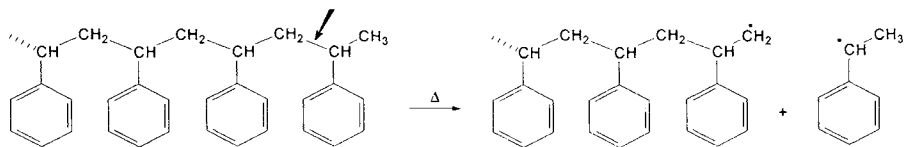
The radical formation may occur by breaking a weaker bond in the molecule, but also by the cleavage of any bond in the chain. The formation of two radicals in a scission reaction is also known as a homolysis.

A typical weaker bond compared to the other of an organic molecule is a sp^3 bond to a carbon next to a double bond, a triple bond, or an aromatic ring (e.g. $\text{C} \rightarrow \text{C}=\text{C}$). These bonds are indicated as in β -position and are in general weaker than other C-C or C-H bonds and significantly weaker than aromatic, double, or triple bonds. The scission of this type of sp^3 bond is known as β -scission. The β -scission can take place as a

random β -scission or as an end chain β -scission. Random β -scissions may take place with the formation of one free radical chain plus one low molecular weight free radical different from the monomer or may consist of two free radical chains when the cleavage takes place in the middle of the polymeric chain, as shown below.

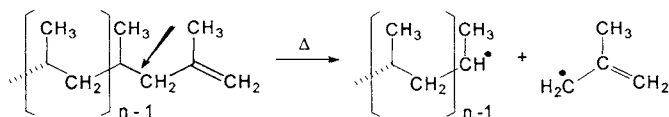


Since larger free radicals are more stable than those with small molecules, the fragmentation in the middle of the polymeric chain is favored thermodynamically compared to the formation of small molecules. However, kinetic factors also may play a role in determining the abundance of a specific compound. The formation of small radicals from the end of a polymeric chain can be kinetically favored, and, as a result, formation of small radicals in the initiation step is more common than expected based on the thermodynamic criteria. Taking as an example polystyrene, an end chain β -scissions to the aromatic ring can be written as follows:



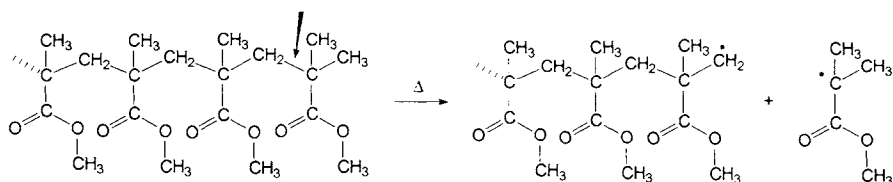
(The scission in the β -position to the carbon with unsatisfied valence is also common during the propagation reaction). The bond to the methyl group at the end of the chain is also in the β position to the aromatic ring, and the formation of a CH_3^\bullet radical also is possible. However, the energy required to form a CH_3^\bullet radical is usually higher than that of the formation of a larger fragment. A more detailed discussion regarding the bond dissociation energy is given in Section 2.2.

For some polymers, the double bond may be present only at the end of the molecule. For example, for polypropylene the end chain β -scission does not generate the monomer and takes place as follows:



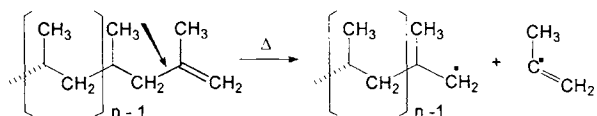
The presence of double bonds at the end of the polymeric chain and the relatively lower stability of the bond in a β position to the double bond increases the probability of the end scission compared to random scissions in many polymers.

The β -scission may take place not only in the β position of a $C=C$ double bond, but also in the β position relative to a double bond involving heteroatoms (such as O, S, N). For example, the initiation step at the end of the molecular chain for methyl methacrylate can be written as follows:



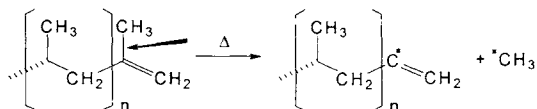
The chain scission also can start truly randomly and not only at the weaker bond. For polymers containing linear backbones, in addition to β -scissions, it is possible to have α -scissions, methyl scissions or even hydrogen scissions. The scission of a $C-H$ bond is thermodynamically unfavorable at low temperatures and is not too common at temperatures where the other scission can take place. The α -scission is more frequent. It refers to the breaking of a σ bond to an sp^2 carbon. For polystyrene for example, the α -scission leads to the formation of a phenyl radical and a polymeric radical (and it is not a chain scission).

Using the example of polypropylene, the α -scission can occur only at the end of the polymeric chain and takes place as follows:



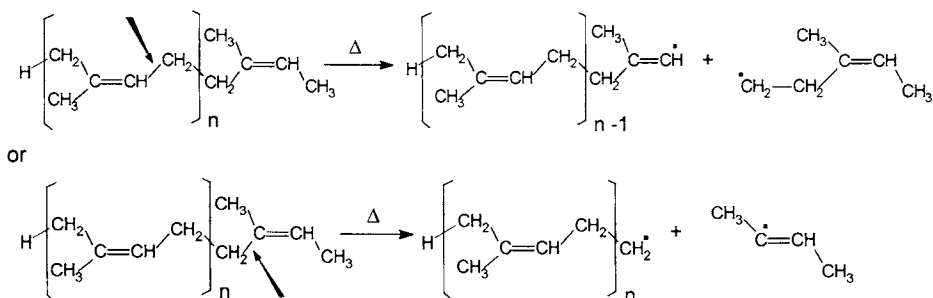
The radical $\text{CH}_2=\text{CH-CH}_2^\bullet$ is more stable than the radical $\text{CH}_2=\text{C}^\bullet\text{-CH}_3$ formed in the above scission and a rearrangement probably takes place.

A methyl scission at the end of the polymeric chain can be written as follows:

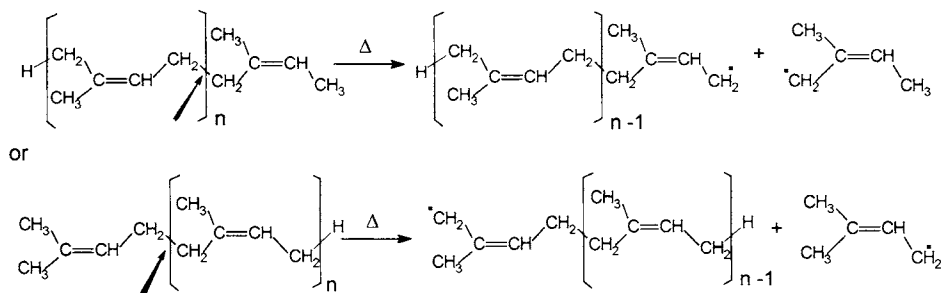


As shown by these reactions, the end group of a polymer may play an important role in the initiation of the radicalic elimination reaction.

For polymeric chains with various groups, more than one α -scission, β -scission, or methyl scission may take place. For example, in the case of polyisoprene, the α -scission (shown for the end of the chain) may take place in the following two ways:



The β -scission may take place in the following two ways:



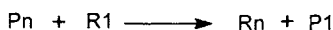
The bond dissociation energy for the α -scission is 83–94 kcal mol⁻¹, and for the β -scission is 61.5 – 63 kcal mol⁻¹. The radical formation is therefore more likely to occur as a β -scission. For polyisoprene decomposition, the methyl scission initiation is also possible, and the bond dissociation energy is similar to that for α -scission. For polymers with more than one methyl group, more than one type of free radical can be formed. The mechanism of the first step in the chain scission followed by a particular polymer depends on both thermodynamic and kinetic factors, which will be further discussed in Sections 2.2 and 2.3.

In addition to the initiations previously indicated, the traces of oxygen molecules, hydroperoxide side groups, and residual peroxide catalysts that are still present in a polymer structure may be sites for the pyrolysis initiation reaction. These initiations usually do not affect the final composition of the pyrolysates, but they may affect the temperature where the pyrolysis process starts. For example, pyrolysis in the presence of traces of air (oxygen) typically occurs at temperatures 50° C to 100° C lower than pyrolysis in pure He.

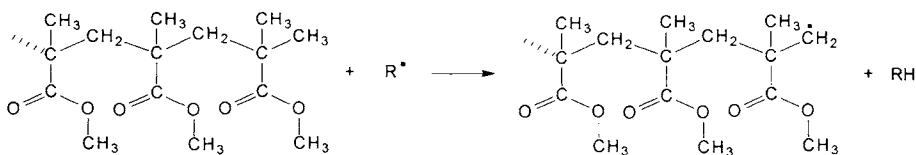
In conclusion, the initiation reaction caused by heat can be a complex process, and more than one type of free radical formation can occur during pyrolysis. This adds complexity to the pyrolysis process, which may generate a significant number of different pyrolysis products even from a polymer with a simple structure.

- Propagation reactions during the chain scission in pyrolysis

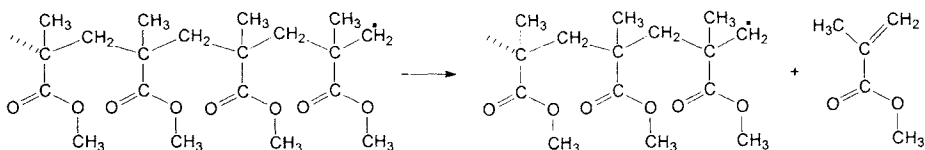
Propagation is the second step in the free radical chain reaction. This step leads to new radicals but also to the formation of small stable molecules. Because the stability of a long chain free radical is usually higher than that of a small free radical, if small radicals are formed in the first step, they usually react with the polymer, forming polymeric chain radicals and small molecules. This type of propagation is known as radical transfer reaction. Using the notation P_n for the polymer and R_n for the polymeric radical, the radical transfer reactions can be indicated as follows:



As an example, for poly(methyl methacrylate), the radical transfer reaction may take place as follows:

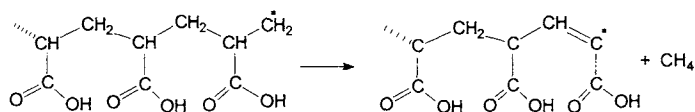


The propagation reaction may continue with the elimination of small molecules from the polymer radical, as shown below:

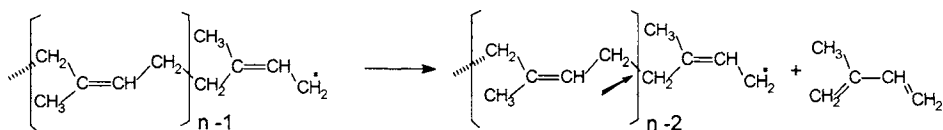


The elimination takes place at the β -position to the atom with unpaired electrons. The formation of the monomer from the polymeric radical is sometimes indicated as "unzipping." Since small molecules are stable, this reaction may be the main process during the pyrolysis of certain polymers. The high yield of monomer in the pyrolysis of methyl methacrylate is generated mainly from this reaction.

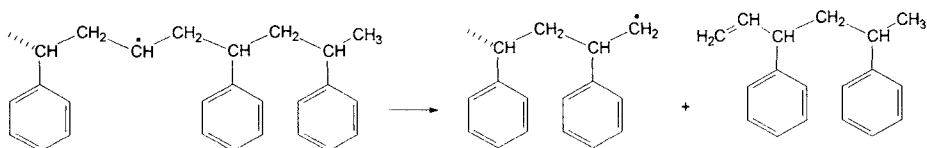
In some cases, an elimination also can occur at the α -position with the formation of small molecules such as CH_4 , NH_3 , etc. An example is shown below for acrylic acid (see Table 6.7.1).



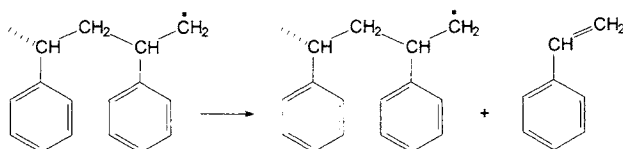
For polyisoprene the monomer can be generated with scission even further than two atoms from the one bearing the radical, by the following propagation reaction:



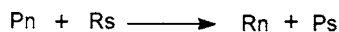
The radicals shown in the previous examples contain the odd electron atoms at the end of the radical chains. This is the most common case, since the radicals containing the unpaired electron in the middle of the polymeric chain tend to suffer disproportionation and form radicals with the odd electron at the end of the chain, as shown below for polystyrene:



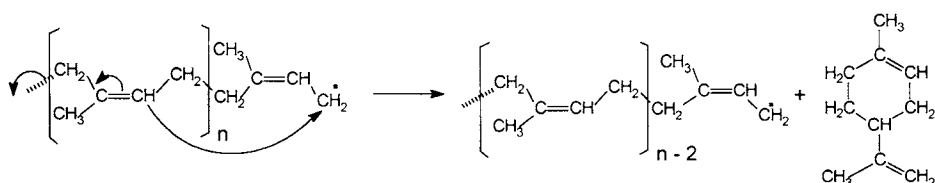
The depolymerization reaction with the formation of monomers is favored by the formation of the free radical with the odd electron at the end of the chain, and reactions as shown below are typical in polymer decomposition:



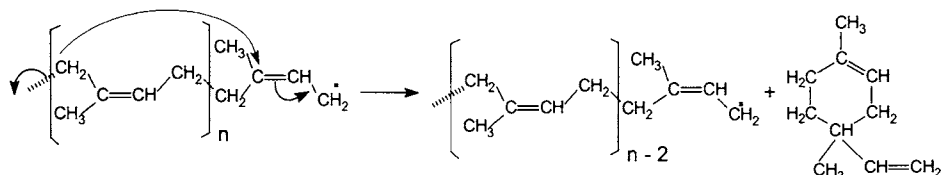
The radical transfer reaction, instead of occurring from a small radical to a large molecule, may occur randomly, and one radical may generate a different radical chain and a new polymeric molecule. This type of chain transfer of an unpaired electron from one molecule to another is known as *intermolecular transfer*, which can be written as follows:



For the case of polystyrene, this type of reaction can be written as follows:



Other cyclic dimers can be formed by the following scheme:



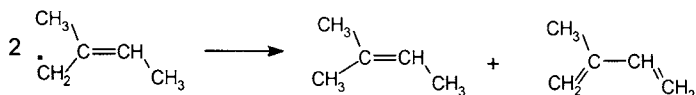
The modification of a radical by reacting with a certain point of its own chain (also indicated as "bite back") and elimination of a cyclic compound is a common type of propagation reaction. It takes place in many pyrolytic processes when the steric structure of the molecule allows the reaction, when the eliminated molecule is favored energetically (e.g. aromatic rings), and when the reactivities of specific centers in the molecule are active. The kinetic factors are in general more difficult to estimate, but the probability of a efficient collision with another large molecule may be lower than that with the own chain of the radical, which also favors the bite back reactions.

- Termination reactions during the chain scission in pyrolysis

Termination is the last step in a radicalic chain scission process generated by heat. The radical reactions can be terminated by disproportionation or recombination. The disproportionation reaction can be schematically written as follows:



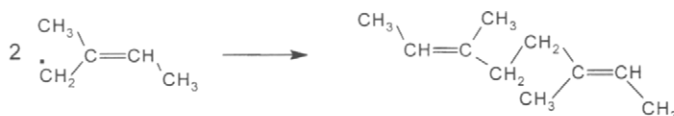
For example, in the case of isoprene (in the case of $n=1$), the disproportionation occurs as follows:



The recombination reactions can be written as follows:



For the case of isoprene and for $s = 1$ and $n = 1$, two free radicals will react as follows:



The same types of reactions may take place for the free radical chains. Either a disproportionation or a recombination may take place. In the discussion of the examples chosen above, not all the possibilities were considered.

The yield of monomer formation from the polymer upon pyrolysis does not give a good indication which mechanism is followed from the initiation to the termination reactions since various routes may lead to the same final monomer yield. Regardless the mechanism, the formation of the monomer as a final product is usually indicated as *depolymerization*. The yield of monomer from pyrolysis for various polymers is shown in Table 2.1.1. The decomposition temperatures for each polymer may be different.

TABLE 2.1.1. The yield of monomer during pyrolysis (different temperatures) for various polymers.

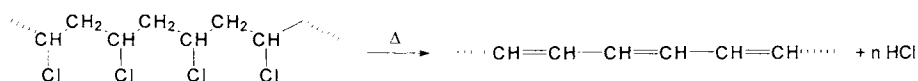
Polymer	Monomer yield weight %
poly(methyl methacrylate)	95
poly(methyl acrylate)	2
poly(α -methylstyrene)	95
poly(m -methylstyrene)	45
polystyrene	42
polyisoprene (natural rubber)	up to 58
poly(isobutylene)	20
polypropylene	2
polyethylene (linear)	0.1
polyethylene (branched)	0.025
poly(vinylcyclohexane)	0.1
polytetrafluoroethylene	95
poly(trifluorostyrene)	75
poly(trifluorochloroethylene)	28
poly(trifluoroethylene)	1
poly(vinylidene fluoride)	1
poly(vinyl fluoride)	1
poly(p -xylylene)	0
polybenzyl	0
poly(vinyl chloride)	1

In many instances the random cleavage of the polymeric chain leads to the formation of oligomers, but this scission is typically followed by secondary reactions. If the oligomers are further decomposed to the monomer level, the overall reaction is still indicated as depolymerization. However, for some polymers such as methylsilicones, the oligomers formed through random chain scission further react, leading to a variety of compounds such as cyclic oligomers. In this case, the pyrolysis reaction is indicated as *random scission*.

- Side group reactions

Side group reactions are common during polymer pyrolysis, and they should take place before the chain scission [8]. The presence of water and carbon dioxide as main pyrolysis products in numerous pyrolytic processes can be explained by this type of reaction. The reaction can have either an elimination mechanism or it can have a substitution mechanism. Side eliminations are common for many linear polymers. However, because these reactions generate smaller molecules but do not affect the chain of the polymeric materials, the heating continues to affect the chain. Therefore the initial reactions may be continued with chain scission reactions, and the end result appears as combined types of reactions.

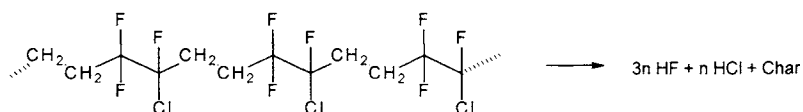
An example of side chain reaction is given below for poly(vinyl chloride):



Similar reactions are given by polyvinyl acetate with elimination of acetic acid, poly(vinyl ethers) with elimination of alcohols, etc. The most common case for these reactions is the β -elimination with two groups lost from adjacent atoms, usually taking place with an E_1 mechanism, although E_2 and E_1 mechanisms are not excluded.

The polyene chain further decomposes under the influence of heat, generating aromatic hydrocarbons such as benzene, styrene, naphthalene, etc. This type of reaction can be the source of some polycyclic aromatic hydrocarbons found in traces during the pyrolysis of certain vinyl polymers. The elimination of a HX molecule from a vinyl type polymer is favored by the presence of a β -double bond in a compound of the form $-\text{CH}_2-\text{CHX}-\text{CH}=\text{CH}-$. For this reason the side reaction for vinyl polymers is slower for the intact polymer and accelerates as the polymer tends to decompose.

The elimination of a HX molecule is also typical for a polymer such as poly(ethylene-*alt*-chlorotrifluoroethylene). In this case the elimination reaction from the side chain takes place as follows:



The thermogram of the polymer obtained in N_2 indicates a 67.36% loss during heating and 31.99% residue as shown in Figure 2.1.1. Considering the polymer molecular formula $(\text{C}_4\text{H}_4\text{F}_3\text{Cl})_n$, the proportion of C in the molecule is 33.25%. This value is very close to the residue shown in the thermogram, indicating that only a small part of the polymer backbone is transformed in volatile compounds, and most of the carbon is left as char.

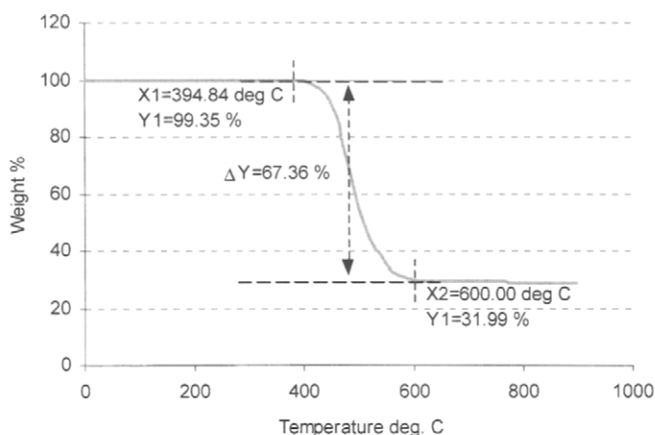
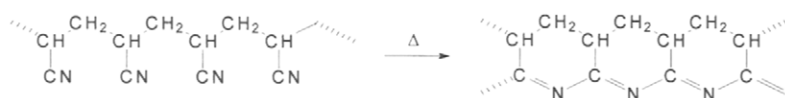


FIGURE 2.1.1. Thermogram in an inert atmosphere of a poly(ethylene-alt-chlorotrifluoroethylene) sample using a heating rate of 10° C/min.

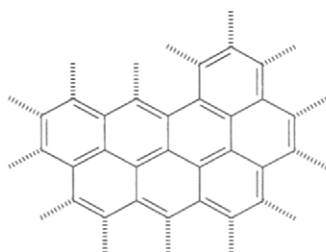
Besides eliminations, other reactions may take place at the side chain. For example, polyacrylonitrile undergoes at 160–300° C in the presence of oxygen a reaction as shown below:



At temperatures above 700° C, the rings in the cyclized polymer eliminate hydrogen and become aromatic. At temperatures above 900° C, the material loses N₂ and generates char made from carbon. Other side chain reactions are discussed in Part 2 of this book.

- Char formation during polymer pyrolysis

Char formation is a common result of side chain reactions that maintain the C-C bonds and eliminate small molecules (such as H₂O, CO₂, etc.) or hydrogen. The formation of polyphenylene structures prior to char formation is common. Certain temperature resistant polymers that typically contain aromatic rings are more prone to the formation of char than other polymers. Pure graphite can be represented by an ideal formula as shown below:



However, most polymers will form more complicated residual materials, containing some hydrogen, five ring cycles, or groups residual from the original polymer. In general, the result is indicated as carbonization and occurs as a sequence of reactions of different types that are not clearly understood for most polymers. Various studies regarding the structure of char (carbonized polymers) are reported in literature [9].

- Combined reactions during pyrolysis

As shown previously, it is uncommon that the side chain reactions will take place independently from any chain scission. Heating at relatively low temperatures between 100° C to 300° C (known as thermal degradation) may lead in some polymers to side chain reactions with elimination of small molecules (such as H₂O, HCl), while the polymer backbone still remains intact. At typical pyrolysis temperatures (500–800° C) both types of reactions occur simultaneously or very rapidly one after the other, as combined reactions. Combined reactions may take place either with a cyclic transition state or with free radical formation. The free radicals formed during polymeric chain scission or during the side chain reactions can interact with any other part of the molecule.

Pyrolytic reactions can appear to be much more complicated compared to other reactions. However, this is mainly due to subsequent reactions that occur after the initial elimination step. A common cause of this problem is related to the fact that the reactions do not actually take place in ideal gas phase. Some pyrolytic processes may take place in true condensed phase. Multiple reaction paths and the interaction of the resulting molecules are, therefore, inevitable. Also, additional issues may affect the practical results of a pyrolysis. Some are related to the fact that the true pyrolysis can be associated with reactions caused by the presence (intentional or not) of non-inert gases such as oxygen or hydrogen that may be present during the heating. Also, the pyrolyzed materials may be in contact with non-inert surfaces that can have catalytic effects. In order to diminish these effects in the pyrolysis done for analytical purposes, an inert gas frequently is present during the pyrolytic reaction.

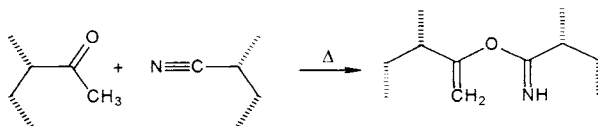
- Interactions in the pyrolysis of copolymers

The considerable importance of copolymers for practical purposes generated a considerable number of studies dedicated to thermal stability and pyrolysis of copolymers (see e.g. [10–15]). The presence of two or more monomeric structures in a macromolecule can influence significantly the thermal behavior and the composition of its pyrolysate. Depending on the ratio of the comonomers, as well as on the structure of the polymer (*random*, *alt*, *block*, *graft*, etc.), the pyrolysis output can be very different. Based on this, pyrolysis results are frequently used for the analysis of copolymer structures.

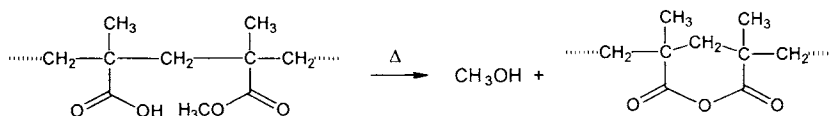
Depending on the copolymer structure, the frequency of fragments containing more than one type of monomeric unit can be an important indication of the copolymer structure. For example, an *alt*-copolymer contains only AB type dimers, and no AA or BB ones.

Random copolymers will have all three types of dimer molecules, while block copolymers will have a small number of AB dimers and mostly AA and BB dimers. The subject will be discussed further in Section 4.2.

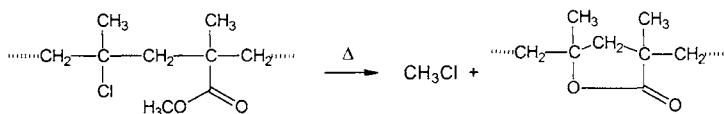
Regarding the influence of chemical composition on copolymer pyrolysis, this can be different from copolymer to copolymer. In some cases, the decomposition is not affected significantly by the other comonomer, and pyrolysis has a path analogous with that for individual homopolymers [16]. In other cases, the influence is considerable [8]. The influence on one monomer type by the other can be seen in the generation of new products or in the rate of decomposition. One example with generation of new products is that of polyacrylonitrile containing methylvinylketone. Neighboring groups may undergo, under the influence of heat, reactions as indicated below:



The resulting polymer generates by pyrolysis a variety of fragments including amides, which can be explained by the decomposition of structures as previously indicated. Another example is the high yield of methanol in the pyrolysis of poly(methacrylic acid-co-methyl methacrylate), with the reaction shown below:



A similar process takes place during the formation of CH_3Cl in the pyrolysis of poly(vinyl chloride-co-methyl methacrylate):



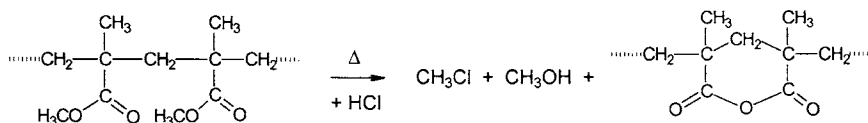
The influence in the decomposition rate has been seen for example in the poly(styrene-co-acrylonitrile) copolymers. The elimination of HCN from the side chain of the polymer generates double bonds in the backbone. The decomposition of the polymer is significantly accelerated in this case, since the cleavage of the backbone in the β -position to the double bond is facilitated [17]. In other cases, such as in the copolymers of methylmethacrylate with acrylonitrile, the rate of decomposition is decreased around 220°C and the yield of monomer diminished [18].

Decomposition kinetics can be influenced by different mechanisms that depend on the copolymer structure. A number of specific cases will be discussed in Part 2 of this book.

- Co-pyrolysis of polymers

Simultaneous pyrolysis is sometimes performed for two (or more) independent polymers together. This is a relatively common process encountered in practice either during pyrolysis of polymer blends or during pyrolysis of different mixtures of polymers as found, for example, in different types of waste (see Section 5.1). For this reason, several studies were dedicated to polymer co-pyrolysis [19–22]. Some of these studies were performed for mixtures of synthetic and natural polymers [23, 24]. In many instances, the co-pyrolysis does not generate, at noticeable levels, any compounds that contain moieties from two (or more) polymer types. The mixing of two polymers involved in co-pyrolysis is usually done only at macroscopic scale and large regions of the sample consist of a unique polymer. The result for these co-pyrolysis experiments is a superposition of compounds from each polymer pyrolysate but with no interaction. However, interactions may occur, mainly in gas phase after the initial pyrolysis of the polymers, and for these cases there are compounds in the pyrolysate that show origin from two different polymers. For example, co-pyrolysis of poly(vinyl chloride) and poly(ethylene terephthalate) leads to the formation of some chloroesters of terephthalic and benzoic acids [19]. Also, co-pyrolysis of polyacrylonitrile with coal-tar pitch shows interaction compounds. The principal chemical interaction during thermal degradation at 300° C of this mixture takes place as a hydrogen abstraction from pitch constituents by radicals generated from polyacrylonitrile (PAN) bonds scission [20].

Some studies show that pyrolysis of certain polymer blends can be influenced by the migration of a small molecule or a small radical formed from one type of polymer and affecting the other type. For example, poly(methyl methacrylate) (PMMA) in blends with poly(vinyl chloride) (PVC) shows higher resistance to heat. The thermal decomposition of PVC generates HCl, which interacts with the PMMA forming anhydride units in the middle of PMMA chains, as shown below:



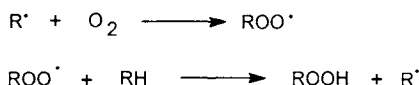
The anhydride units interrupt the unzipping process characteristic for PMMA pyrolysis. A similar effect may have the free radicals generated during the decomposition of one polymer and interacting with the other one in a blend.

In a wider sense, pyrolysis of many mixtures can be viewed as co-pyrolysis. Most examples come from the pyrolysis of polymers in the presence of a solid material such as carbon black (used extensively in tire industry), metal oxides, pyrolysis of reinforced plastics (for example with glass fibers), pyrolysis of polymer impregnated concrete, etc. [25]. In these cases, the pyrolysis of carbon, of metal oxide, of glass fiber, or of concrete does not generate any particular small molecules. However, the pyrolysis of the synthetic polymer may be influenced by the structure of the additional ingredient. For example, carbon black exhibits no influence on the decomposition of poly(methyl methacrylate) (PMMA), which has quaternary carbon atoms in the polymer chain and decomposes by depolymerization. The decomposition of polypropylene (PP) in the presence of carbon black is promoted, whereas, that of polyethylene (PE), polystyrene (PS) and PAN is hindered [26, 27].

- Pyrolysis in the presence of reactive gases or with catalysts

Pyrolytic reactions, mainly for analytical purposes, are commonly done in a helium atmosphere. Sometimes these reactions are done, intentionally or not, in the presence of additional reactants or in the presence of catalysts. The most common additional reactants are probably oxygen, hydrogen, and water (gas at pyrolysis temperature). Oxygen from the air and water are sometimes unintentionally present during pyrolysis. The presence of an additional reactant can modify the result of the pyrolytic reaction, either qualitatively or quantitatively.

Oxygen can be a participant in the pyrolysis in two different ways: it can be present as atmospheric oxygen, or it may be already reacted with part of the sample in an autoxidation process by exposure of the sample to air and light over a period of time. In the presence of excess air and at temperatures above the flaming point of the utilized material, burning and not pyrolysis will take place. Although burning is commonly associated with secondary pyrolytic processes, this is not the subject of interest here. The results of the pyrolytic process in the presence of air (below the flaming temperature) can be seen more like a vacuum pyrolysis catalyzed by oxygen [28]. In this type of situation, the pyrolysis products are not significantly different from those obtained without oxygen, but the rate of the reaction is different. However, traces of oxidations also may occur. Free oxygen has an unusual molecule. In its ground state each of the two highest occupied molecular orbitals, which are degenerated, contain unpaired electrons (a triplet state of the molecule). This means that ordinary oxygen has the properties of a diradical. This diradical can react with other radicals in a chain oxidation as follows:



In an excited electronic state (singlet oxygen) oxygen is much more reactive. The oxygen in a singlet state can be generated by a photochemical reaction and may react with a wide variety of materials by a so-called autoxidation process. The singlet oxygen may react with the double bond forming a dioxetane intermediate:



Polymers exposed to air and light may contain oxidized groups such as peroxides ($\sim\text{OOR}$). The O-O bond is weak (30–50 kcal/mol) and, upon heating, dissociates to form free RO^\bullet radicals and radical polymeric chains. These radicals may influence the composition of the pyrolysis products. Autoxidation may take place in food, paint, rubber, etc. It is important, therefore, to consider this possibility when evaluating the composition of the pyrolysis products of a material that was exposed to air and light although the pyrolysis is performed in an inert gas. Pyrolysis in the presence of a controlled proportion of oxygen (such as 2%–3%) may be used for studying different materials [29].

Pyrolysis in the presence of hydrogen has been done with the purpose of modifying the chemical composition of the pyrolysate [30]. In principle hydrogen can react with numerous chemical compounds. However, molecular hydrogen as such is not very reactive. In most chemical reactions, only the hydrogen generated directly in the reaction medium is active (e.g. from Zn and HCl). Pyrolysis in molecular hydrogen proceeds in most cases in a manner similar to the pyrolysis in an inert gas (helium or nitrogen). In order to make use of the hydrogen reactivity, a catalyst must be used. Common catalysts are metals such as platinum or nickel. In analytical pyrolysis, hydrogen and a catalyst can be used with the purpose of diminishing the number of species resulting in pyrolysis. When the pyrolytic process is followed by a chromatographic separation, the chromatogram of the pyrolysate (the pyrogram) can appear to be too complicated. If this pyrogram consists, for example, of groups of compounds with the same carbon chain but containing single and multiple bonds, this can be simplified by hydrogenation. For each group of compounds, only the saturated one will appear after a catalytic hydrogenation. The procedure can be useful only in some particular cases, and it is not commonly used.

The presence of water as a reaction product from the pyrolytic processes or as adsorbed water on the material to be pyrolyzed is not unusual. However, in analytical pyrolysis, water is not commonly added to the sample. During some pyrolytic processes with industrial applications such as wood pyrolysis, water is sometimes added intentionally. The main effect of water during pyrolysis is hydrolysis. This takes place as the temperature elevates and can be seen in the modification of the yields of different final pyrolysis products. Therefore, the reproducibility in analytical pyrolysis may be influenced by the variability of water content of the initial sample [31].

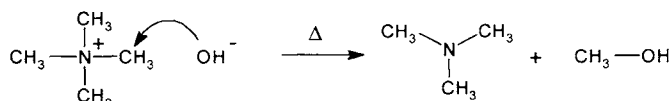
Carbon black also was found to influence certain pyrolysis reactions. It has been shown [26] that in a mixture polymer/carbon black the nature of substituents on the hydrocarbon chain of the polymers affects the thermal behavior. Carbon black exhibits no influence on the decomposition of poly(methyl methacrylate), which has quaternary carbon atoms in the polymer chain and decomposes by depolymerization. The decomposition of polypropylene is promoted, whereas that of polyethylene, polystyrene and polyacrylonitrile is hindered in the presence of carbon black. The char yield of polyacrylonitrile is increased significantly. However, carbon black has no impact on the amount of residue of non-char-forming polymers. Analysis of the pyrolysis products indicates that carbon black has influence through the chain cleavage and H-transfer reactions. The promotion of the chain scission reactions in polypropylene is indicated by the lower decomposition temperature and the increased formation of products originating from the primary macroradicals. It appears that carbon black participates in the termination of the chain reactions, and the yield of oligomers is significantly reduced from the vinyl polymers. The increased yield of hydrogenated products also confirms the role of carbon black in the H-transfer reactions.

- Pyrolysis/alkylation

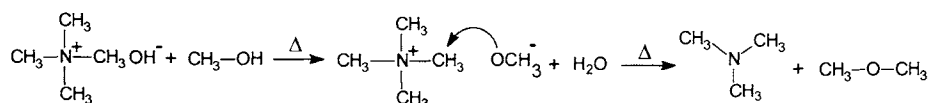
One of the problems during the analysis of pyrolysates using chromatographic techniques is that polar compounds such as larger acids are not easily eluted from

typical chromatographic columns. In-situ derivatization is one of the solutions to this problem. Several attempts were made to perform in-situ silylation, but the results are still modest. The silylation reaction is not rapid enough, and a delay period between pyrolysis and analysis is usually necessary for the reaction to take place. Better results are obtained by performing pyrolysis in the presence of quaternary N-alkyl (or alkyl, aryl) ammonium hydroxides [32–36]. The procedure was initially applied by the addition of the reagent in the hot injection port of a gas chromatograph for the methylation of acidic components from a sample, and later with different pyrolytic techniques by directly adding tetramethyl ammonium hydroxide (TMAH) together with the material to be pyrolyzed [37, 38]. The derivatization reagents are applied on the sample either as an aqueous solution (e.g. for tetramethyl ammonium hydroxide) or as methanolic solutions. Not only tetramethyl ammonium hydroxide is used as a derivatization reagent during pyrolysis. Other quaternary N-alkyl (or alkyl-aryl) ammonium hydroxides are successfully used as derivatization reagents. Such reagents are tetrabutyl ammonium hydroxide [38], phenyltrimethyl ammonium hydroxide (or trimethyl anilinium hydroxide), (m-trifluoromethylphenyl)trimethyl ammonium hydroxide or trimethyl-trifluoro-m-tolyl ammonium hydroxide [39], etc. Also, other pyrolytic derivatizations with the formation of ethyl, propyl, hexyl, etc. derivatives are known.

During pyrolysis, quaternary ammonium hydroxide is also decomposed. For example, the decomposition of tetramethyl ammonium hydroxide occurs by the following reaction:

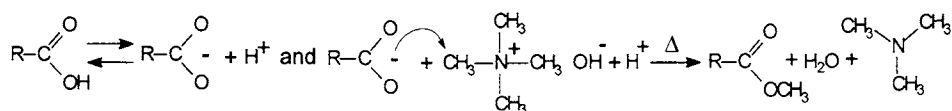


Methanol and trimethylamine are therefore found in the pyrograms in addition to the compounds generated from the sample. Other small molecules can be generated from the reagent. For example, dimethyl ether can be formed by the following reaction:

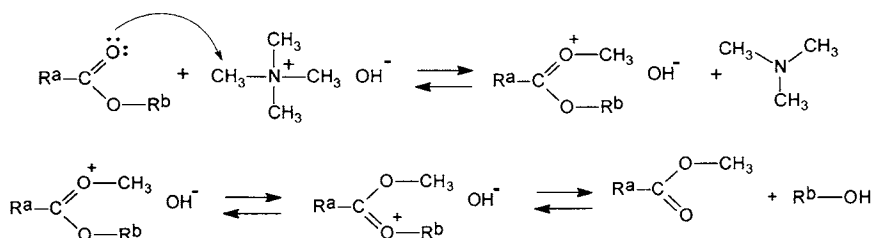


Similarly, anisole is formed during the decomposition of phenyltrimethyl ammonium hydroxide.

The methylation of the acids formed in the pyrolysate is probably a simple reaction as shown below:



Methylation derivatization also has been successfully used for the transmethylation of esters and carbonates. For an ester, the reaction can take place by the following mechanism:



The mechanism of formation of methyl esters from polyesters can be simpler, not involving the formation of an intermediate compound. Pyrolysis of ester type polymers in the presence of quaternary ammonium hydroxides such as TMAH may occur by the following simple steps: a) the polymer when mixed with TMAH and heated to temperatures around 400° C undergoes hydrolysis because of the strong basic character of the reagent, b) TMAH salts of the hydrolyzed products are formed, c) the salts undergo thermal fragmentation to the methyl derivatives [40].

Although pyrolysis in the presence of TMAH generates methylated compounds, it has been shown that off line methylation of the pyrolysis products may not be identical to the products of pyrolysis in the presence of the methylating reagent [41]. Some hydrolysis type reactions or other reactions that do not occur in simple pyrolysis take place in the presence of TMAH. The presence of other reactions besides thermal decomposition and methylation does not occur in the same manner for all samples. This is true for synthetic polymers, but it was fully proven for several natural polymers. For example, the pyrolysis/methylation reported for lignin shows fewer unexpected reactions compared for example with the case of carbohydrates [42]. The phenolic compounds generated from lignin are easily methylated, being sufficiently acidic, and lignin is more resistant to basic hydrolysis and does not react in itself with TMAH. For other natural polymers such as cellulose, pyrolysis in the presence of TMAH is far from equivalent with the methylation of the compounds generated from the simple pyrolysis of cellulose, and the process is typically known as thermochemolysis. In other cases, only part of the pyrolysate is methylated and part remains not methylated. The strong basic character of substituted ammonium hydroxide type reagents puts some limitations to their use. For this reason, the use of tetramethylammonium fluoride (TMAF), phenyltrimethylammonium fluoride or phenyltrimethylammonium acetate as pyrolytic methylation reagents without the additional effect of the basic character of TMAH is very promising [41]. The pyrolysis in the presence of methylating/hydrolysis reagents such as TMAH is more and more utilized during the pyrolysis of compounds that have acidic groups [43, 44] or ester groups. In one such study performed on aromatic polyesters, it has been shown that the solvent for TMAH also may play a role in the reaction during pyrolysis. The use of deuterated methanol as a solvent for TMAH showed that the solvent is involved in a methanolysis process [45].

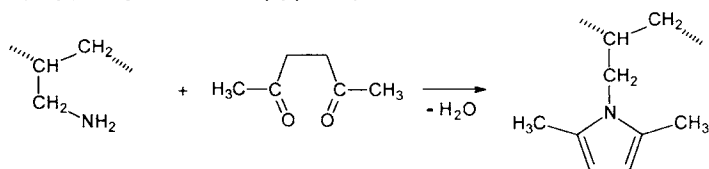
- Acid and alkali fusion of polymers

Analysis of many polymers can be performed after they are transformed into small fragment molecules by using chemical cleavage of certain bonds in the polymer. This

chemical cleavage is typically done using heating in addition to reagents. For example, crosslinked epoxy resins can be hydrolyzed using acid fusion with acetic anhydride/ acetic acid with reflux at 120° C [46] for 30 min. Further analysis by a GC technique of the hydrolysate is then possible. Other polymers require even harsher conditions for cleavage. A variety of hydrolysis resistant polymers were analyzed by GC techniques following fusion with a mixture of potassium hydroxide and 5% sodium acetate at temperatures between 250° C and 300° C [47]. Acid or alkali fusion has been used in the analysis of polyvinyl derivatives [48], polymethacrylates [49], polyacrylamide and polyacrylonitrile [50], polyesters [51], polycarbonates [52], nylons [53, 54], aramides [55], polyimides [56, 57], polysulfones [58], polyurethanes [59–64], polysiloxanes [65–69], polycarborane siloxanes [70], etc. However, these techniques can be only marginally classified as pyrolysis. For this reason, no further detailed descriptions of such techniques are included in this book.

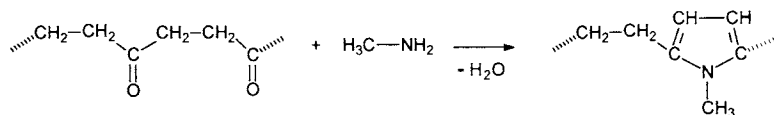
- Pyrolysis after polymer derivatization

Analytical pyrolysis of certain polymers and copolymers do not provide too much relevant information because of the rapid decomposition of the groups specific to that polymer. For example, the copolymers with maleic anhydride (see e.g. Sections 5.1 and 5.9) generate mainly CO₂ from the maleic anhydride units. For the identification and for other studies on these types of polymers or copolymers, a polymer derivatization prior to pyrolysis can be applied [71]. For example, poly(allylamine) can be derivatized with acetonylacetone in a water solution by adding a NaOH. The reaction leads to the formation of poly(N-allyl-2,5-dimethylpyrrole) as shown below:



Pyrolysis of the resulting polymer provides more information on the initial polymer structure than the pyrolysis of the underivatized polymer.

Another example where polymer derivatization prior to pyrolysis provides benefits regarding structural information is that of poly(ethylene-*alt*-carbon monoxide) (see Section 5.8). This copolymer can be derivatized with methyl amine in a reaction as follows:



Pyrolysis of the resulting polymer generates a series of pyrrole derivatives diagnostic for the nature of the copolymer. Similar derivatization with methylamine can be performed on copolymers containing maleic anhydride [72].

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2.2 THERMODYNAMIC FACTORS IN POLYMER FORMATION AND DECOMPOSITION

- General aspects

Description of thermochemical properties of chemical compounds, including that of polymers can be done using a few thermodynamic functions. One basic function is Gibbs free enthalpy that is expressed as follows [1]:

$$G = H - TS \quad (2.2.1)$$

where G is the free enthalpy, H is the enthalpy, T is the absolute temperature, and S is the entropy. The enthalpy H is further expressed by the formula:

$$H = E + pV \quad (2.2.2)$$

where E is internal energy, p is the pressure and V is the volume. In differential form these expressions are written as follows:

$$dG = dH - TdS - S dT \quad (2.2.3)$$

$$dH = dE + pdV + V dP \quad (2.2.4)$$

The first law of thermodynamics for a closed system (which does not exchange energy or mass with its surroundings) is expressed in the form:

$$dE = dQ + dW \quad (2.2.5)$$

where Q is the heat and W the work; and for a reversible system, the second law of thermodynamics is expressed by:

$$dQ - TdS = 0 \quad (2.2.6)$$

For systems with the work resulting from volume modifications, the value of dW is expressed by the formula:

$$dW = -pdV \quad (2.2.7)$$

Using rel. (2.2.4) through (2.2.7) in the expression giving the variation of free enthalpy, rel. (2.2.3) becomes:

$$dG = Vdp - SdT \quad (2.2.8)$$

For open systems with "r" components suffering changes, rel. (2.2.8) is modified in the form:

$$dG = Vdp - SdT + \sum_{j=1}^r dn_j \mu_j \quad (2.2.9)$$

where n_j is the number of moles and μ_j is the chemical potential of component "j". The chemical potential can be defined as the molar free enthalpy of a pure substance, or

$$\mu_j = \left. \frac{\partial G}{\partial n_j} \right|_{T,p,n_{1,2}} \quad (2.2.10)$$

where the index $T, p, n_{1,2}, \dots$ indicates constant temperature, pressure and number of moles of the other components.

In a multicomponent system, the partial molar quantities for a component "i" in a phase can be defined for any extensive thermodynamic function Z (enthalpy, energy, entropy, etc.). The partial molar quantity Z is the change in Z for a change in n_i or

$$Z = \partial Z / \partial n_i \quad (2.2.11)$$

Partial molar quantities are intensive thermodynamic functions. For example, the partial molar volume is the increase of the volume per mole of component "i" when the number of moles of "i" are modified with an infinitesimal amount. Thus, the partial molar volume of component "i" is given by the expression:

$$\left. \frac{\partial V}{\partial n_i} \right|_{T,p,n_j} = V_i \quad (2.2.12)$$

On the other hand, from rel. (2.2.9) $V = \left. \frac{\partial G}{\partial p} \right|_{T,n}$, and therefore between V_i and μ_i , there is the following relation:

$$V_i = \left. \frac{\partial \mu_i}{\partial p} \right|_{T,n_j} \quad (2.2.13)$$

In equilibrium conditions, and using the ideal gas law, rel. (2.2.13) is equivalent with the expression:

$$d\mu_i = RT \frac{dp_i}{p_i} \quad (2.2.14)$$

where p_i is the partial pressure of the component "i" and R is the gas constant ($R = 8.31451 \text{ J deg}^{-1} \text{ mol}^{-1} = 1.987 \text{ cal deg}^{-1} \text{ mol}^{-1}$). The integration of rel. (2.2.14) leads to the expression:

$$\mu_i = \mu_i^0 + RT \ln (p_i / p_i^0) \quad (2.2.15)$$

where p_i^0 is the (vapor) pressure of a pure liquid "i" (at the equilibrium temperature T), and μ_i^0 is the standard chemical potential for the compound "i".

For any isolated (closed) system, spontaneous transformations take place with an increase in the entropy ΔS of the system (see e.g. [2]). For a nonisolated system in isothermal conditions, spontaneous processes take place with a negative variation of free enthalpy ΔG where:

$$\Delta G = \Delta H - T \Delta S + \sum_{j=1}^r n_j \mu_j \quad (2.2.16)$$

where G is given by rel. (2.2.1), ΔH is the variation in enthalpy of the system, T is measured in Kelvin degrees ($0^\circ \text{ K} = -273.15^\circ \text{ C}$) and ΔS is the variation in entropy of the system. From rel. (2.2.16) for ΔG and based on the fact that a spontaneous process takes place with a negative variation of free enthalpy ΔG , it can be seen that in a spontaneous process a system will have the tendency to lower its enthalpy (or at constant volume its energy $\Delta E = \Delta H - p \Delta V$) and to increase its entropy.

For a system with r components at constant temperature and pressure as shown by rel. (2.2.9), the total free enthalpy is defined as the sum of the chemical potentials and:

$$\Delta G = \sum_{i=1}^r n_i \mu_i \quad (2.2.17)$$

The expression for μ_i as a function of standard chemical potential is given by the expression rel. (2.2.15), which being used in rel. (2.2.17) generates the following expression:

$$\Delta G - \Delta G^0 = RT \sum_{i=1}^r n_i \ln(p_i) \quad (2.2.18)$$

where ΔG^0 is the standard free enthalpy (noted 0) at constant pressure of 1 atm. Since ΔG^0 is a function of temperature alone, the sum in rel. (2.2.18) is a constant.

For a transformation at constant pressure p and temperature T , equilibrium will correspond to a minimum of the free enthalpy. Otherwise, the process would spontaneously continue. For equilibrium, the following expression can be written for the closed system:

$$\delta G = 0 \quad \text{or} \quad \Delta G = 0 \quad (2.2.19)$$

and rel. (2.2.18) will become:

$$\Delta G^0 = - RT \sum_{i=1}^r n_i \ln(p_i) \quad (2.2.20)$$

Considering now a chemical reaction at the equilibrium:



where "A", "B", ... are different molecular species, the following expression can be written between the partial pressure of the gases in the mixture:

$$K_p = \frac{p_D^d p_E^e \dots}{p_A^a p_B^b \dots} \quad (2.2.22a)$$

where p_A is the partial pressure of the component A, p_B is the partial pressure of the component B, etc. Including K_p given by rel. (2.2.22) in rel. (2.2.20), it can be easily seen that the following expression is valid:

$$\Delta G^0 = - RT \ln K_p \quad (2.2.23)$$

Since ΔG^0 is a constant, K_p is also constant and is known as the equilibrium constant for the reaction (2.2.21).

For ideal gases the partial pressure p_X for the component X can be related to the molar concentration $[X]$ by the expression $p_X = (RT) [X]$. The equilibrium constant for the reaction (2.2.21) can be written using concentrations instead of partial pressures in the form:

$$K_c = \frac{[D]^d [E]^e \dots}{[A]^a [B]^b \dots} \quad (2.2.22b)$$

where the relation between K_c and K_p is given by the expression:

$$K_c = K_p (RT)^{-\Delta n} \quad (2.2.24)$$

and $\Delta n = d + e + \dots - a - b - \dots$ and represents the number of moles of products minus the number of moles of reactants in the stoichiometric equation for the reaction.

For negative values of ΔG^0 , the reaction equilibrium is displaced toward the formation of reaction products, and reactions with negative ΔG^0 occur spontaneously.

The free enthalpy accompanying the reaction is the difference in the standard free enthalpies of the products and the reactants. Similar expressions are true for the enthalpy and the entropy of the system with expressions given below:

$$\Delta G^0 = \sum \Delta G^0_{\text{products}} - \sum \Delta G^0_{\text{reactants}} \quad (2.2.25a)$$

$$\Delta H^0 = \sum \Delta H^0_{\text{products}} - \sum \Delta H^0_{\text{reactants}} \quad (2.2.25b)$$

$$\Delta S^0 = \sum \Delta S^0_{\text{products}} - \sum \Delta S^0_{\text{reactants}} \quad (2.2.25c)$$

Because ΔG^0 , ΔH^0 , and ΔS^0 are temperature dependent, they must be given at a certain temperature. For many chemical compounds the values for ΔH^0 and ΔS^0 are known (see e.g. [3]). The expression for ΔG^0 can be obtained easily using the well-known formula:

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (2.2.26)$$

However standard values are typically provided for 298.15° K, while pyrolysis reactions take place at much higher temperatures. A more rigorous treatment should apply the following corrections:

$$\Delta H^0_T = \Delta H^0_{298} + \Delta C^0_p (T - 298.15) \quad (2.2.27a)$$

$$\Delta S^0_T = \Delta S^0_{298} + \Delta C^0_p \ln (T/298.15) \quad (2.2.27b)$$

where ΔC^0_p is the average variation in the heat capacity and is given by the expressions:

$$\Delta C^0_p = (\Delta C^0_{p,T} + \Delta C^0_{p,298})/2 \quad (2.2.28a)$$

where the heat capacities at different temperatures are given by:

$$\Delta C^0_{p,T} = \sum \Delta C^0_{p,T} \text{ products} - \sum \Delta C^0_{p,T} \text{ reactants} \quad (2.2.28b)$$

This correction seems not to be able to resolve the problem of temperature dependence of ΔH^0 and ΔS^0 . However, ΔC^0_p is typically small and its effect on ΔH^0 and ΔS^0 tend to compensate each other. For this reason, in much estimation for thermochemical values at elevated temperatures, the values for 298.15° K are used. The index for ΔH^0 and ΔS^0 indicating the temperature is not necessary when $T = 298.15^\circ \text{ K}$.

- Free enthalpy in formation of polymers

Formation of polymers is governed by thermodynamic and kinetic factors (see also Section 2.3). The free enthalpy of polymerization is an important parameter, which is known for various monomers. Tables with values for ΔH^0 and ΔS^0 are given in literature [4]. Several values for ΔH for the formation of some polymers having in the backbone chain only carbon atoms are given in Table 2.2.1 (1 cal = 4.1868 J international, 1 cal = 4.184 J thermochemical). Some of the values are given for ideal gas phase, although few monomers and no polymers are in gas phase. Since in a reaction the reactant and the product can be in different aggregation states, the state of both participants must be indicated.

The values for the thermodynamic parameters in the formation of polymers can be used for the characterization of depolymerization reactions. The formation of monomers in a polymer decomposition reaction (depolymerization) is relatively common (see Table 2.1.1). Depolymerization can be considered a reverse polymerization, the two reactions having equal absolute values for the heats of reaction but with opposite signs. Therefore, the heats of polymerization can be used for the thermodynamic characterization of pyrolytic reactions with formation of monomers (kinetic factors are also very important in pyrolytic reactions as further shown in Section 2.3).

TABLE 2.2.1. *Heats of formation for a number of polymerization reactions generating carbon atoms chains* [4]. The aggregation state for the monomer and for the polymer (ideal) are indicated as follows: g = gas, l = liquid, c = solid crystalline, a = solid amorphous, s = solution.

Monomer	State*	$-\Delta H^0$ kcal/mol	Temp °C	Monomer	State*	$-\Delta H^0$ kcal/mol	Temp °C
1,3-butadiene	gg (a)	17.45	25	methacrylamide	lc	10.16	74.5
"	gg (b)	18.64	25	methacrylic acid	lc	10.16	74.5
"	lc	17.45	25	"		15.42	25
chloroprene	lc	16.25	61.3	methacrylic acid methyl ester	lc	13.38	130
isoprene	gg	16.85	25	"	lc	13.26	74.5
"	lc	17.93	25	"		13.15	25
ethylene	gg	22.35	25	methacrylonitrile	lc	13.50	74.5
"	ga	25.93	25	vinyl chloride	gc	31.55	25
propene	gg	20.67	25	"	lc	16.97	25
"	ga	24.86	25	vinyl acetate	ls	23.54	25
1-butene	gg	20.67	25	"	ss (f)	21.51	74.5
"	ga (c)	25.81	25	vinylidene chloride	la	18.04	25
isobutene	gc	17.21	25	"	la	14.34	76.8
"	lc (d)	11.47	25	styrene	gg	17.81	25
acrylamide	lc	18.98	90	"	lc	16.73	25
acrylic acid	lc	16.01	74.5	"	lc	17.45	127
acrylic acid n-butyl ester	lc	18.64	74.5	α -methyl styrene	lc	8.37	25
acrylic acid methyl ester	lc	18.64	76.8	2-vinylpyridine	lc	17.09	74.5
acrylonitrile	la	18.28	74.5	4-vinylpyridine	lc	18.64	74.5
"	sa (e)	18.52	74.5				

* (a) 1,2-polymerization, (b) 1,4-polymerization, (c) isotactic polymer, (d) low MW, (e) in benzene, (f) in acetone.

- Bond dissociation energy from thermochemical data

Modeling of an entire pyrolytic process is a difficult task, which requires the consideration of both thermodynamic and kinetic factors. This subject will be further discussed in Section 2.4. However, specific aspects of the thermal decomposition do not necessarily require the understanding of the whole pyrolysis process. Evaluation of *bond dissociation energy* is a typical application of thermochemical information related to the prediction of pyrolysis mechanism and indirectly of pyrolysis outcome. Using bond dissociation energies it is possible, for example, to estimate the temperature where the thermal degradation starts. As shown in Section 2.1, a common mechanism found to operate in pyrolytic reactions is the elimination involving free radicals. For this reaction, the initiation starts with a pyrolytic cleavage. The temperature where the thermal degradation starts can be predicted considering only this pyrolytic cleavage. In a polymer there are many different bonds, which may be of the same type, or different. In a single polymer chain, thermal energy will distribute itself relatively rapidly so that all of the bonds in the macromolecule are exposed to the same energy. The bond that will break first is likely to be the one that is the weakest link in the chain. Although the fragmentation in pyrolysis does not take place only at the weaker bond, the weaker bonds typically have higher probability of breaking. This indicates that the thermal stability of a polymer can be estimated from the energy of the weakest bond in the polymer chain.

Since the energy and enthalpy are equal at constant pressure and volume, from rel. (2.2.4) and (2.2.5) it can be seen that in these conditions $\Delta E = \Delta H = \Delta Q$. The bond dissociation energy equals the negative value for the heat of formation of the bond ΔH_f° (A-B) and is a direct measure of the bond strength. The reaction of bond dissociation can be written as follows:



Based on rel. (2.2.25b) the enthalpy of bond dissociation is given by the expression:

$$\Delta H_f^\circ (\text{A-B}) = \Delta H_f^\circ (\text{A}^\cdot) + \Delta H_f^\circ (\text{B}^\cdot) - \Delta H_f^\circ (\text{AB}) \quad (2.2.29)$$

Several average bond energies (evaluated at 25° C) for different bond types are given in Table 2.2.2.

TABLE 2.2.2. Average bond energies at 298.15° K in kcal/mol [5]

Bond	$-\Delta H_f^\circ (\text{A-B})$ kcal/mol	Bond	$-\Delta H_f^\circ (\text{A-B})$ kcal/mol
O-H	110-119	C-Br	66
C-H	96-99	C-S	61
N-H	93	C-I	52
S-H	82	C=C	199-200
C-O	85-91	C=C	146-151
C-C	83-85	C=N	204
C-Cl	79	C=O	173-181
C-N	69-75	C=N	143

In addition to the nature of the atoms forming the bond, the bond strength depends on the rest of the molecule. The values from Table 2.2.2 give only an estimate for a specific bond strength. More precise bond dissociation energies can be given when the nearest neighbors of the dissociating bond are specified. Table 2.2.3 gives the estimated bond energies in kcal/mol at 298.15° K when the molecular moiety is considered for the bond strength.

TABLE 2.2.3. Bond dissociation energies at 298.15° K in kcal/mol considering the nearest neighbor in different molecular moieties [6-9].

Group-	Energy kcal/mol								
	-group -H	-F	-Cl	-Br	-I	-CH ₃	-C ₂ H ₅	-CH ₂ R	-CHR ₂
H-	104.2								
F-	136.4	38.0							
Cl-	103.2	60.0	57.1						
Br-	87.5	56.2	52.1	45.4					
I-	70.7	52.1	49.7	43.0	35.6				
CH ₃ -	104.2	108.3	84.1	70.0	56.2	88.2			
C ₂ H ₅ -	101.0	106.0	81.0	69.1	53.1	84.5	81.6		
R-CH ₂ -	98.2	106.1	81.0	69.1	53.1	85.1	81.4	80.5	
(CH ₃) ₂ CH-	98.5								
R ₂ CH-	94.2	105.2	81.0	67.6	53.1	83.2	80.2	78.2	76.0
(CH ₃) ₃ C-	96.5								
R ₃ C-	91.1	102.1	79.1	63.1	50.2	80.1	76.9	75.0	73.1
CH ₂ =CHCH ₂ -	88.0								
Ph-	111.1	125.2	100.1	80.1	65.0	94.0	90.6	91.1	83.2
Ph-CH ₂ -	88.5	90.1	68.1	51.1	40.2	72.2	76.0	62.1	55.0
Ph(CH ₃)CH-	86.0								
Ph(CH ₃) ₂ C-	84.0								
Ph ₂ CH-	79-82								
1,3-cyclohexadiene	76.0								
CH ₂ =CH-allyl-	109.0		86.0		55.0	90.1	90.0	90.1	85.1
CH≡C-	86.8					73.6	70.3	70.3	67.7
CH(O)CH ₂ -	133.0					100.1		109.2	103.2
CF ₃ -	92-95								
FCH ₂ -	106.1	129.3	85.1	70.0	54.0	100.1			
CCl ₃ -	101.0								
ClCH ₂ -	96.1	106.1	73.1	54.0					
HO-	100.0								
CH ₃ O-	119.3					91.1		91.1	92.0
RO-	103.0								
PhO-	102.1	59.0	49.0			80.1		80.1	81.0
HOCH ₂ -	87.0						67.0		
HO(CH ₃)CH-	96.0								
CH ₃ OCH ₂ -	94.0								
-CH(O)-	93-94.5								
CH ₃ C(O)-	87.2					75.0		71.0	
RC(O)-	89.0								
HOC(O)CH ₂ -	86.0		82.2	67.2	51.1	82.2		77.2	
HOC(O)-	94-97.5								
HC(O)O-	92.5								
HC(O)O-	105.0								

TABLE 2.2.3 (continued). Bond dissociation energies at 298.15° K in kcal/mol considering the nearest neighbor in different molecular moieties [6-9].

Group-	-group	-H	-F	-Cl	-Br	-I	-CH ₃	-C ₂ H ₅	-CH ₂ R	-CHR ₂
CH ₃ C(O)O-		104-106								
RC(O)O-		112.1								
CH ₃ OC(O)CH ₂ -		93-98								
CH ₃ OC(O)-		92.5								
NH ₂ -		106.0					79.1		78.2	77.2
H ₂ NCH ₂ -		93.5								
CH ₃ NH-		99.0								
RNH-		92.0								
PhNH-		85-93						70-77		
(CH ₃) ₂ N-		91.5								
R ₂ N-		86.0								
CN-							110.2			
SH-		90.1								
RS-		88.2		65.0						

Group-	-group	-CR ₃	-Ph	-CH ₂ -Ph	-CH=CH ₂	-C≡CH	-CF ₃	-CCl ₃	-OH	-OR
R ₃ C-		70.0								
Ph-		78.2	115.0							
Ph-CH ₂ -			77.2	56.01						
CH ₂ =CH-		81.0	101.1	70.0	112.1					
allyl-				58.0	78.4					
CH=C-			119.3			110.2				
CF ₃ -							97.0			
CCl ₃ -								87.2		
HO-		91.1	112.1	77.2					51.1	
RO-		78.2	101.1							33.9
-CH(O)			90.1	50.2						
RC(O)-				63.1					44.0	
-C(O)O-				55.0						
NH ₂ -		77.2	100.1	65.0						
CN-			130.3	95.1	121.2					

Group-	-group	-CH(O)	-C(O)R	-OC(O)R	-NHR	-NR ₂	-CN	-SH	-SR
CH(O)-		60.0							
RC(O)-		60.0	60.0						
RC(O)O-		59.0		30.1					
NH ₂ -		90.1	98.2						
RNH-					37.0				
R ₂ N-						42.1			
CN-							145.3		
SH-								30.1	
RS-									63.1

Even considering the next neighbor it is not always possible to obtain a good estimation of the dissociation energy and additional corrections must be made. For example, when the dissociating bond is in conjugation with a π electron system, the dissociation energy must be decreased with about 16 kcal/mol for a phenyl ring and with about 10 kcal/mol for a double bond. Also, the number of carbons in an aliphatic radical R, as indicated in Table 2.2.3, plays a considerable role in the value of bond dissociation. The higher the

number of carbon atoms in R, the lower is the dissociation energy. The data from Table 2.2.3 offer guidance regarding the fragmentation of polymers. Extensive information on bond dissociation energies can be found in literature [10].

The values for ΔH° (A-B) indicated in Table 2.2.3 lead to some observations regarding bond stability. For example, for the strength of a C-H bond, the increase in the π -character of the adjacent bond leads to an increase in the C-H bond strength. From Table 2.2.3, it can be noticed the following values: 133 kcal mol⁻¹ for CH₃C-H, 111.1 kcal mol⁻¹ for Ph-H, 109 kcal mol⁻¹ for CH₂=CH-H, and 101.0 kcal mol⁻¹ for C₂H₅-H. Similar observations show decrease in the strength for the series CH₃-H > CH₃CH₂-H > (CH₃)₂CH-H > (CH₃)₃C-H, and also for the series PhCH₂-H > PhCHR-H > PhCR₂-H. The effect on the second carbon is opposite. The bond strength decreases in the series: CH₃CH₂-H > PhCH₂-H > CH₂=CHCH₂-H > Ph₂CH-H. For bonds between two carbon atoms, similar tendencies can be noticed by inspecting Table 2.2.3. For the bonds to heteroatoms, the strength increases with the increase in the atomic number in the order CH₃-H < NH₂-H < HO-H < F-H. The trend is maintained when one of the hydrogens on the main atom is replaced with alkyl groups.

When the enthalpy for the homolytic dissociation of the bond A-B is not known, it can be derived [11] from tabulated heats of formations ΔH_f° of the AB compound and from that of free radicals A[•] and B[•] using rel. (2.2.29). The values for ΔH_f° (AB) are available for many compounds [3, 14–19], and some values for small molecules are given in Table 2.2.4 [20].

TABLE 2.2.4. Enthalpies of formation kcal/mol and entropies cal/T/mol for several small molecules in ideal gas form at 298.15° K.

Small molecule	Molecule name	ΔH_f° kcal/mol	ΔS° cal/T/mol	Small molecule	Molecule name	ΔH_f° kcal/mol	ΔS° cal/T/mol
H ₂	hydrogen	0.0	31.23	C ₄ H ₆	1,3-butadiene	26.3	68.58
N ₂	nitrogen	0.0	45.79	C ₄ H ₁₀	2-methylpropane	-32.1	70.4
O ₂	oxygen	0.0	49.03	C ₆ H ₆	benzene	19.8	64.36
O ₃	ozone	34.1	57.1	C ₆ H ₅ -CH ₃	toluene	12.0	76.65
NO	nitrous oxide	21.38	50.37	p-C ₆ H ₄ (CH ₃) ₂	p-xylene	4.3	84.32
NO ₂	nitrogen dioxide	7.91	57.34	C ₆ H ₅ -CH=CH ₂	styrene	35.3	82.51
SO ₂	sulfur dioxide	-70.95	59.32	CH ₂ =CH-CN	acrylonitrile	43.16	14.5
SO ₃	sulfur trioxide	-94.59	61.37	HF	hydrofluoric acid	-65.14	41.53
CO ₂	carbon dioxide	-94.05	51.1	HCl	hydrochloric acid	-22.06	44.67
CO	carbon monoxide	-26.42	47.24	HBr	hydrobromic acid	-8.71	47.49
H ₂ O ₂	hydrogen peroxide	-32.6	55.63	HI	hydroiodic acid	6.3	49.37
(CN) ₂	dicyan	73.86	57.73	HCN	hydrocyanic acid	32.3	48.21
C ₂ F ₄	tetrafluoroethylene	-223.03	62.48	H ₂ O	water	-57.8	45.11
CH ₄	methane	-17.9	44.51	H ₂ C=O	formaldehyde	-26.0	52.31
C ₂ H ₂	ethyne (acetylene)	54.54	47.98	HCOOH	formic acid	-90.5	59.44
C ₂ H ₄	ethene (ethylene)	12.55	52.47	NH ₃	ammonia	-11.0	46.03
C ₂ H ₆	ethane	-20.03	54.87	H ₂ S	hydrogen sulfide	-4.9	49.17
C ₃ H ₆	propene	4.78	63.84	CH ₃ -COOH	acetic acid	4.78	67.52
C ₃ H ₈	propane	-25.02	64.53				

Tables with heats of formation for radicals also are available in literature (e.g. [12, 13]). Some enthalpies of formation and some entropies for a number of common free radicals are given in Table 2.2.5.

TABLE 2.2.5. Enthalpies of formation kcal/mol and entropies in cal/T/mol at 298.15° K for some common free radicals [13].

Radical	Name	$\Delta H_f^\circ(A\cdot)$ kcal/mol	$\Delta S^\circ(A\cdot)$ cal/T/mol	Radical	Name	$\Delta H_f^\circ(A\cdot)$ kcal/mol	$\Delta S^\circ(A\cdot)$ cal/T/mol
H \cdot	hydrogen radical	52.1	-11.8	CH $^{\cdot}$ -OH	hydroxymethylene	27.2	
F \cdot	fluorine radical	19.1	-13.6	CH ₃ O \cdot	methoxy	-3.0	
Cl \cdot	chlorine radical	28.9	-12.9	CH ₃ CO \cdot		-3	
Br \cdot	bromine radical	26.8	-23.7	C ₂ H ₅ O \cdot	etoxy	-5.0	
I \cdot	iodine radical	25.6	-26.8	C ₆ H ₅ O \cdot	phenoxy	12.0	
OH \cdot	hydroxyl radical	9.5	-1.4	HO(O)C \cdot	HOOC radical	50.0	
CH $^{\cdot}$	methylidyne	142.4		HC(O)O \cdot	formate radical	-38.0	
CH ₂ $^{\cdot}$	methylene	92.3		CH ₃ COO \cdot	acetate radical	-49.5	
CH ₃ \cdot	methyl	34.8	46.4	HC(O)CH ₂ \cdot		0.0	
CH ₂ =CH \cdot	vinyl	69		HOC(O)CH ₂ \cdot		-61.5	
HC \equiv C \cdot	ethynyl	135		CH ₃ C(O)OCH ₂ \cdot		-55.0	
CH ₃ -CH $^{\cdot}$	methylmethylene	90.3		NH ₂ \cdot		44.0	
CH ₃ -CH ₂ \cdot	ethyl	29.0	43.9	H ₂ NCH ₂ \cdot		36.0	
(CH ₃) ₂ CH \cdot	isopropyl	21.5		CN \cdot	cyanide	104.0	-15.1
CH ₂ =CH-CH ₂ \cdot	allyl	41.0		CH ₃ -NH \cdot	CH ₃ -NH radical	41.5	
CH ₃ -CH ₂ -CH ₂ \cdot	propyl	21.0		(CH ₃) ₂ N \cdot		34.5	
CH ₃ -CH \cdot -CH ₃	2-propyl	16.8		C ₆ H ₅ -NH \cdot		58.0	
CH ₃ -(CH ₂) ₂ -CH ₂ \cdot	butyl	16.0		CF $^{\cdot}$	fluoromethylidyne	61.0	
C ₂ H ₅ -CH \cdot -CH ₃	2-butyl	12.0		C(O)F \cdot	COF radical	-42.3	
(CH ₃) ₂ -CH-CH ₂ \cdot	i-butyl	13.0		CHO \cdot	HCOF radical	-90.0	
(CH ₃) ₃ -C \cdot	tert-butyl	12.5		FCH ₂ \cdot		-7.0	
C ₆ H ₅ \cdot	phenyl	79.0		ClCH ₂ \cdot		28.0	
C ₆ H ₅ -CH ₂ \cdot	benzyl	48.5		CF ₂ $^{\cdot}$	difluoromethylene	-45.0	
C ₆ H ₅ (CH ₃)CH \cdot		41.0		CF ₃ \cdot	trifluoromethyl	-112.4	
C ₆ H ₅ (CH ₃) ₂ C \cdot		33.0		CF ₃ -CH ₂ \cdot	CF ₃ -CH ₂ radical	-123.6	
(C ₆ H ₅) ₂ CH \cdot		66.5		CCl $^{\cdot}$	chloromethylidyne	111.3	
C ₆ H ₇ \cdot		50		CHCl $^{\cdot}$	chloromethylene	80.0	
CH ₃ -CO \cdot	methylcarbonyl	-5.0		COCl \cdot	COCl radical	-15.0	
CH ₃ -CO-CH ₂ \cdot	propanonyl	-12.0		CCl ₂ $^{\cdot}$	dichloromethylene	57.0	
CHO \cdot	HCO radical	10.5		CCl ₃ \cdot	trichloromethyl	21.0	
HOCH ₂ \cdot		-4.0		CBr ₃ \cdot	tribromomethyl	64.7	
CH ₃ OCH ₂ \cdot		-3.0		Cl ₃ \cdot	triiodomethyl	117.3	
HO(CH ₃)CH \cdot		-14.5					

A simple example for the calculation of the bond energy between a hydrogen atom and the carbon in ethane (C₂H₅-H) would lead to the following calculation: ΔH_f° (H \cdot) = 52.1 kcal/mol, ΔH_f° (C₂H₅ \cdot) = 25.0 kcal/mol ΔH_f° (C₂H₆) = -20.03 kcal/mol, and the resulting bond energy is ΔH_f° (C₂H₅-H) = 52.1 + 25 - (-20.03) = 97.13 kcal/mol, in very good agreement with the value from Table 2.2.3 of 98.0 kcal/mol.

Using rel. (2.2.29) it is possible to estimate the dissociation energy for larger molecules. The first step is the calculation of the values for AB. As an example, using experimental data for the heat of formation of normal hydrocarbons (see e.g. [3]), it is possible to generate the following correlation equation for the heats of formation (see also Figure 2.2.4):

$$\Delta H_f^0 (C_n H_{2n+2}) = -4.90 n - 10.97 \text{ kcal/mol} \quad (2.2.30)$$

The heats of formation for the radicals $C_n H_{2n+1}^\cdot$ with n up to about 20 can be obtained in a similar manner using the correlation equation:

$$\Delta H_f^0 (C_n H_{2n+1}^\cdot) = 0.1 n^2 - 9.91 n + 45.05 \text{ kcal/mol} \quad (2.2.31)$$

Combining rel. (2.2.7) with rel. (2.2.8) and using the value for H^\cdot , CH_3^\cdot , $C_2H_5^\cdot$ given in Table 2.2.4, the dissociation energy for $C_n H_{2n+1}-H$, $C_{n-1} H_{2n-1}-CH_3$ and $C_{n-2} H_{2n-3}-C_2H_5$ can be calculated for various normal aliphatic hydrocarbons when the number of carbons n increases. Rel. (2.2.29) for $C_n H_{2n+1}-H$ (up to about 20 C atoms) becomes:

$$\Delta H_f^0 (C_n H_{2n+1}-H) = 0.1 n^2 - 5.01 n + 56.02 + 52.1 \text{ kcal/mol} \quad (2.2.32)$$

The result together with that for $C_{n-1} H_{2n-1}-CH_3$ and $C_{n-2} H_{2n-3}-C_2H_5$ is plotted in Figure 2.2.1 for various n values. For a larger number of C atoms than 20, the value for ΔH_f^0 (A-B) remains practically constant.

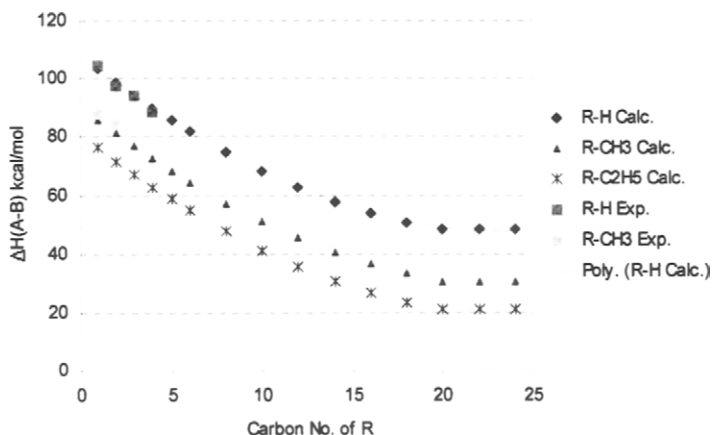


FIGURE 2.2.1. Variation of bond energy $\Delta H_f^0 (C_n H_{2n+1}-H)$, $\Delta H_f^0 (C_{n-1} H_{2n-1}-CH_3)$, and $\Delta H_f^0 (C_{n-2} H_{2n-3}-C_2H_5)$, in kcal/mol with the number of carbons n in normal aliphatic hydrocarbons at $T = 298.15^\circ \text{ K}$. (The calculated values refer to the use of rel. (2.2.29) with experimental data for ΔH_f^0 for $C_n H_{2n+2}$, H^\cdot , CH_3^\cdot , $C_2H_5^\cdot$, and $C_n H_{2n+1}^\cdot$).

The graphs from Figure 2.2.1 show the decrease in the bond energy as the molecule becomes larger and show that beyond a certain molecular mass, the bond energy remains practically constant. Also, the data show that for polyalkanes the bond to a hydrogen atom is stronger than that of a methyl group, which is stronger than that of an ethyl, etc.

Rel. (2.2.30) and (2.2.31) as well as the data from Tables 2.2.3 and 2.2.4 are valid at 25° C, and therefore the results shown in Figure 2.2.1 describe the bond strengths at this temperature. However, for the understanding of the pyrolytic process, the bond strength should be known at temperatures as high as 400–600° C. Since thermodynamic values for higher temperatures are less frequently found in literature, in many cases, estimated data must be used in rel. (2.2.29). This type of estimation can be obtained, for example, using molecular orbital calculations [21, 22]. As an example, the variation of bond energy ΔH_f^0 (R-CH₃) with temperature is shown in Figure 2.2.2 for C₉H₁₉-CH₃. The same figure shows the variation of ΔH_f^0 with temperature for decane, and the radicals nonyl and methyl.

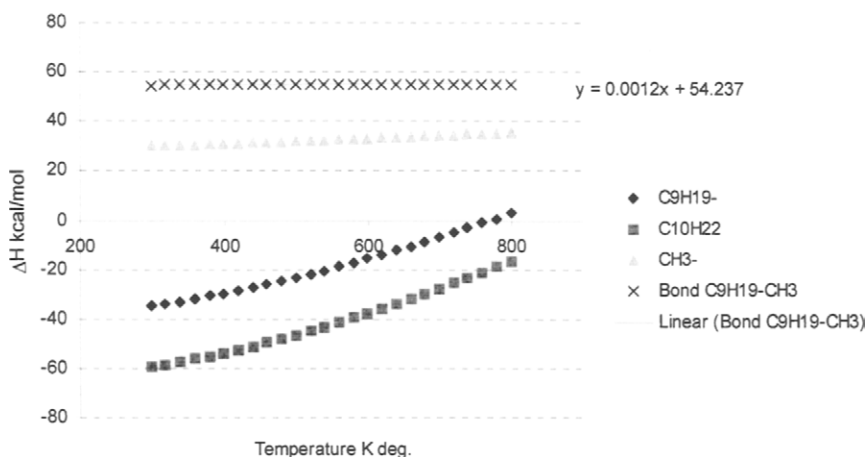
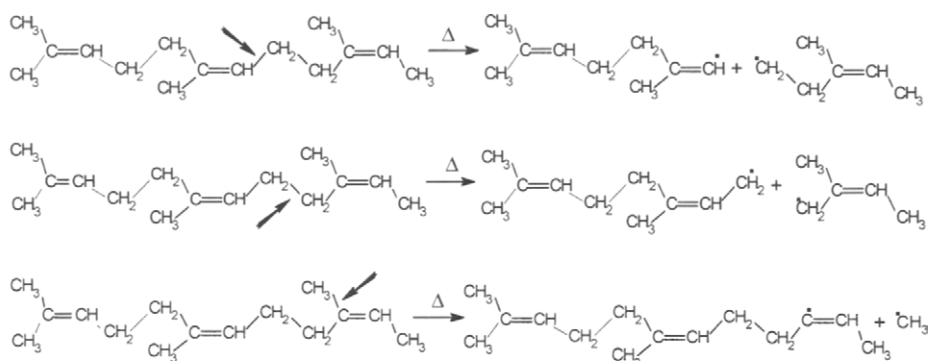


FIGURE 2.2.2. Variation with temperature of the bond energy ΔH_f^0 (C₉H₁₉-CH₃) (kcal/mol). The variation of ΔH_f^0 with temperature for decane, nonyl, and methyl radicals is also shown.

As seen in Figure 2.2.2, the bond energy varies very little with the temperature (practically constant to 54.24 kcal/mol), and the estimation done for 25° C is applicable at much higher temperatures.

An example of a calculation for the evaluation of the bond dissociation energy using rel. (2.2.29) for an isoprene trimer shows the preference for dissociation following a β -scission compared to α - or methyl-scission. The α -scission, β -scission, and methyl-scission are shown below:



The heats of formation for the radicals and for the trimer were estimated using a molecular orbital program MOPAC 7 with AM1 parameterization Hamiltonian for two different temperatures [22]. The calculated bond dissociation energies are given in Table 2.2.6.

TABLE 2.2.6. Bond dissociation energies for an isoprene trimer.

Reaction	Temp. 25° C				Temp. 500° C			
	$\Delta H A^*$ kcal	$\Delta H B^*$ kcal	$\Delta H AB$ kcal	ΔH dissoc.	$\Delta H A^*$ kcal	$\Delta H B^*$ kcal	$\Delta H AB$ kcal	ΔH dissoc.
α scission	46.35	20.69	-18.75	85.79	78.4	43.02	35.33	86.09
β scission	14.96	21.57	-18.75	55.28	50.79	39.9	35.33	55.36
CH ₃ elim.	33.71	31.25	-18.75	83.71	83.16	36.39	35.33	84.22

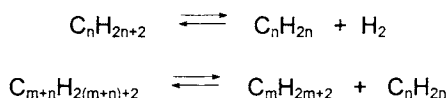
The data from Table 2.2.6 show that during polymer chain scission the initiation reaction is more likely to take place by β scission (lower dissociation energy). Methyl elimination and α scission probably play a less important role in the initiation reaction. These results are in agreement with the experiment. As expected, the values calculated for 25° C and 500° C did not show significant differences.

- Free enthalpy for pyrolytic reactions

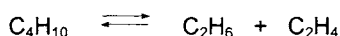
The course of a pyrolytic reaction may be determined kinetically or thermodynamically. When the reaction is able to reach equilibrium, thermodynamic factors control the reaction outcome. The calculation of a reaction free enthalpy using rel. (2.2.25a) allows the prediction of the reaction course. Since reactions are displaced toward the formation of products when $\Delta G^0 < 0$, the calculation of the temperature for which $\Delta G^0 = 0$ allows the determination of which reactions take place and which do not occur at the specific temperature. For pyrolytic reactions, the temperature T satisfying relation $\Delta G^0 = 0$ is defined as the *ceiling temperature* T_c :

$$T_c = \Delta H^0 / \Delta S^0 \quad (2.2.30)$$

Many reactions occurring during pyrolysis involve the breaking of covalent bonds. These reactions are frequently endothermic. For example, pyrolysis of aliphatic hydrocarbons (also pertinent for the pyrolysis of polyethylene) may take place as a dehydrogenation or as a fragmentation. These reactions are shown below:



The reaction with the formation of an alkene is endothermic. In the case of hydrogen elimination, the C–H bond requires considerable energy, and also the breaking of a C–C single bond is not fully compensated by the formation of a new C=C double bond [23]. For a small molecule such as butane, the reaction:



has $\Delta H_{298}^0 = 22.5 \text{ kcal mol}^{-1}$ and $\Delta H_{1000}^0 = 21.5 \text{ kcal mol}^{-1}$ (positive values indicating endothermic reactions). The entropy of the reaction is favorable since the formation of two molecules from one, ($\Delta n = 1$) leads to an increase in entropy. The values for the entropy are $\Delta S_{298}^0 = 33.2 \text{ cal mol}^{-1} \text{ deg}^{-1}$ and $\Delta S_{1000}^0 = 31.5 \text{ cal mol}^{-1} \text{ deg}^{-1}$. Using rel. (2.2.23) at ambient temperature, $\Delta G_{298}^0 = 12.6 \text{ kcal mol}^{-1}$ and $\Delta G_{1000}^0 = -10.0 \text{ kcal mol}^{-1}$. At room temperature (25°C or 298.15°K) the value for the equilibrium constant is $K_p = 5.74 \cdot 10^{-10} \text{ atm.}$, and therefore a very low conversion of butane takes place at equilibrium. At 1000°K (or 827°C) the constant becomes $K_p = 153.3 \text{ atm.}$, indicating a high yield of conversion at equilibrium.

The same type of calculation can be continued for larger hydrocarbons. The enthalpy for any alkane can be obtained from rel. (2.2.30), and a similar correlation relation can be obtained from experimental heats of formation for alkenes (see Figure 2.2.6):

$$\Delta H_f^0 (\text{C}_n\text{H}_{2n}) = -5.01 n + 20.56 \text{ kcal/mol} \quad (2.2.31)$$

The relations for entropies, also obtained from correlation lines using experimental data (see Figure 2.2.5), are the following:

$$\Delta S_f^0 (\text{C}_n\text{H}_{2n+2}) = 9.48 n + 35.77 \text{ cal/mol/deg} \quad (2.2.32)$$

$$\Delta S_f^0 (\text{C}_n\text{H}_{2n}) = 9.50 n + 36.26 \text{ cal/mol/deg} \quad (2.2.33)$$

The expression for the free enthalpy for the dehydrogenation reaction can be written as follows:

$$\begin{aligned} \Delta G^0 &= \Delta H_f^0 - T \Delta S_f^0 = \Delta H_f^0 (\text{C}_n\text{H}_{2n}) + \Delta H_f^0 (\text{H}_2) - \Delta H_f^0 (\text{C}_n\text{H}_{2n+2}) \\ &\quad - T [\Delta S_f^0 (\text{C}_n\text{H}_{2n}) + \Delta S_f^0 (\text{H}_2) - \Delta S_f^0 (\text{C}_n\text{H}_{2n+2})]. \end{aligned} \quad (2.2.34)$$

The result of this calculation is the following:

$$\Delta G^0 = -0.11 n + 31.53 - T 0.032 \text{ kcal/mol} \quad (2.2.35)$$

At low temperature, the reaction has a positive ΔG^0 and therefore does not take place.

The ceiling temperature T_c obtained from rel. (2.2.35) for the dehydrogenation reaction is given by the expression:

$$T_c = \frac{31.53 - 0.11 \cdot n}{0.032} \text{ deg K} \quad (2.2.36)$$

For $n = 10$, for example, the ceiling dehydrogenation temperature is about 670°C .

Following a similar calculation, the free enthalpy for the fragmentation reaction of the molecule $\text{C}_{m+n}\text{H}_{2(m+n)+2}$ to form $\text{C}_m\text{H}_{2m+2}$ and C_nH_{2n} can be expressed as follows:

$$\Delta G^0 = -0.11 n + 20.56 - T 0.036 \text{ kcal/mol} \quad (2.2.37)$$

The ceiling temperature T_c where $\Delta G^0 = 0$ is given by the expression:

$$T_c = \frac{20.56 - 0.11 \cdot n}{0.036} \text{ deg K} \quad (2.2.38)$$

The minimum temperature for which a hydrocarbon generates, for example, decene is about 267°C , and the one for which it generates ethene is 292°C .

The above calculations indicate that the temperature of fragmentation is significantly lower than that of dehydrogenation. Also, it can be noticed that the number of carbon atoms in the molecule ($m + n$) does not affect the course of reaction. The fragmentation temperature seems to be influenced only by the number of carbons of the alkene generated in the reaction. These calculations can be compared with the results from the thermogravimetric analysis of a polyethylene sample. The curve showing the variation of weight loss % as a function of temperature (TG curve) for a polyethylene (high density) sample is shown in Figure 2.2.3 (see also [24]). A 1.5 mg sample was heated between 30°C and 830°C at a heating rate of 10°C/min . in air.

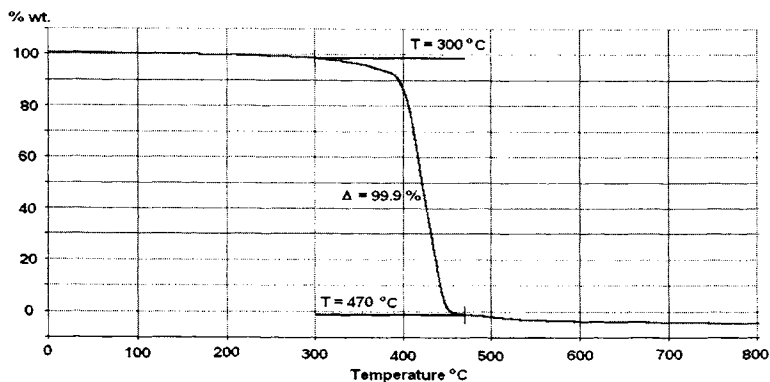


FIGURE 2.2.3. Variation of weight % loss for a polyethylene sample in a TGA experiment at a heating rate of 10°C/min .

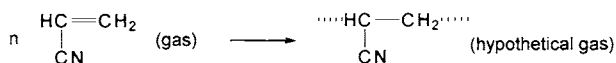
As seen from the thermogram, the weight loss for polyethylene starts around 300°C , which is a slightly higher temperature than the calculated value for the start of fragmentation. When pyrolysis is done at temperatures up to 600°C , very little

dehydrogenation occurs. The presence of alkanes and alkenes with 20–30 carbon atoms is common in polyethylene pyrolysates (see Section 5.1.1), and probably these fragments are formed at lower temperatures, but their volatility not being very high, their formation is not obvious in the thermogram.

Values of thermodynamic functions (heats of formation and entropies) are known for many compounds, typically at 298.15° K = 25° C (see e.g. [17]). However, for even more compounds these values are not known and must be estimated.

- Empirical and estimated values for the free enthalpy

Because of its importance, the estimation of free enthalpy from structural characteristics has been the subject of a significant number of studies [3, 25]. Several procedures can be used for these estimations. One set of procedures is based on quantum chemical methods. These include ab-initio calculations performed with computational packages such as Gaussian 94 [26], semiempirical molecular orbital calculations performed with computational packages such as MOPAC-7 [21, 22, 27, 28], and calculations based on the electron density functions performed with computational packages such as BLYP/DZVP [29–31]. These procedures provide good estimations of various thermodynamic parameters mainly for small molecules and in ideal gas form. However, the calculations can be used to estimate various thermodynamic parameters even for larger molecules. Some attempts also were made to apply quantum chemical calculations to pyrolysis [32]. The applications to larger molecules typically require corrections that are necessary for generating more accurate results [33, 34]. However, even simpler calculations (such as using MOPAC-7) can give relatively good agreement with the experimental values. As an example, for the reaction:



the value for ΔH^0 and ΔS^0 can be calculated using the molecular orbital package MOPAC-7 with a selected parameterization such as AM1 for the Hamiltonian [22]. The results are given in Table 2.2.7.

TABLE 2.2.7. Calculated heats of formation and entropies for acrylonitrile and polyacrylonitrile using MOPAC-7 [22].

Compound/reaction	ΔH kcal/mol	ΔS cal/T/mol	Temp. °C
monomer (calc.)	44.96	14.55	25
monomer (exp.)	43.16	14.5	25
polymer unit syndiotactic (calc.)	20.74	14.69	25
polymer unit isotactic (calc.)	22.86	14.62	25
reaction syndiotactic (calc.)	-24.22	0.14	25
reaction isotactic (calc.)	-22.10	0.07	25
monomer (calc.)	45.72	16.09	75
polymer unit syndiotactic (calc.)	21.52	16.59	75
polymer unit isotactic (calc.)	23.64	16.51	75
reaction syndiotactic (calc.)	-24.19	0.5	75
reaction isotactic (calc.)	-22.05	0.42	75
reaction experimental (liquid/amorphous phases)	-18.28		74.5

The results shown in Table 2.2.7 were calculated for hypothetical stereospecific polymers in gas form, but the results are in fairly good agreement with the experimental values for the heat of reaction.

Another procedure to estimate free enthalpies is based on the assumption that the values for ΔH and ΔS can be obtained from additive fragment contributions with some corrections due to two centers contributions or other structural factors [3, 6]. This type of procedure (additivity model) uses for the estimation formulas of the form:

$$\Delta H^0 = \sum \Delta H_{\text{fragment}}^0 + \sum \Delta H_{\text{structure}}^0 \quad (2.2.39)$$

$$\Delta S^0 = \sum \Delta S_{\text{fragment}}^0 + \sum \Delta S_{\text{structure}}^0 \quad (2.2.40)$$

Individual values for the heat of formation ΔH^0 of fragments in various molecular moieties are given, for example, in [3]. A simplified set of parameters for both heats of formation ΔH^0 and for entropies ΔS^0 of several common fragments in organic molecules and for some structural factors are given in Tables 2.2.8 and Table 2.2.9, respectively. The resulting values are assumed to give estimations for the compounds in ideal gas form [6].

TABLE 2.2.8. Contribution to the heats of formation and to the entropies for several molecular fragments generated in ideal gas form at 298.15 °C [6].

Fragment	$\Delta H_{\text{fragment}}^0$ (kcal/mol)	$\Delta S_{\text{fragment}}^0$ (cal/T/mol)	Fragment	$\Delta H_{\text{fragment}}^0$ (kcal/mol)	$\Delta S_{\text{fragment}}^0$ (cal/T/mol)
-CH ₃	-10.01	22.71	-O-	-23.90	16.73
-CH ₂ -	-5.00	24.38	-HC=O	-29.68	6.21
>CH-	-2.03	28.68	>C=O	-31.91	9.56
>C<	-0.12	33.46	-COOH	-93.93	28.20
=CH ₂	6.29	7.17	-COO-	-80.54	27.72
=CH-	8.51	9.08	-NH ₂	4.52	24.50
=C<	9.70	11.95	-NH-	15.61	28.68
=C=	32.74	-4.78	>N-	24.40	35.85
≡CH	27.17	-7.77	>N _{ar}	16.49	11.95
≡C-	26.94	-5.98	-SH	4.54	7.89
>C _{ar} H	2.99	6.21	-S-	11.09	-5.74
>C _{ar} -	5.98	9.08	>S	14.34	-14.34
>C _{ar} ...	5.02	5.14	-S-S-	10.99	-6.69
-phenyl	20.8	39.91	>S=O	-16.11	15.06
-p-phenylene-	23.9	43.02	-SO ₂ -	-69.14	36.33
-F	-46.61	-1.43	-NO ₂	-7.72	34.18
-Cl	-9.56	-2.15	-ONO	-5.02	31.07
-Br	-1.53	-3.35	-ONO ₂	-21.03	50.91
-I	13.53	-9.80	-NC	49.09	40.8
-CN	25.41	-6.81	-NO	18.09	32.4
-OH	-38.14	11.95			

TABLE 2.2.9. Contributions to the heat of formation and entropy from the combination of two structural factors or from special structure characteristics in molecules in ideal gas form at 298.15 °C [6].

Structural factors		$\Delta H^{\circ}_{\text{structure}}$ (kcal/mol)	$\Delta S^{\circ}_{\text{structure}}$ (cal/T/mol)
-CH ₂ -	=C<	0.31	
-CH ₂ -	-CN	0.95	
>CH-	=C<	0.57	
>CH-	-CN	1.12	
>C<	>C<	3.17	
>C<	=C<	1.86	
>C<	-CN	2.08	
=CH-	=CH-	-1.65	
=CH-	=C<	-1.36	
=CH-	-CN	1.48	
3-atom ring		23.90	-29.16
4-atom ring		23.90	-26.29
5-atom ring		4.78	-23.90
6-atom ring		-0.72	-16.73
conjugated double bonds		-4.30	3.82
cis-trans conversion		-1.43	1.67

For free radicals, some group contributions are given in Table 2.2.10.

TABLE 2.2.10. Contribution to the heats of formation and entropies for several radicals in ideal gas form at 298.15°C [6].

Radical	Name	$\Delta H_f^{\circ}(\text{A}\cdot)$	$\Delta S^{\circ}(\text{A}\cdot)$	Radical	Name	$\Delta H_f^{\circ}(\text{A}\cdot)$	$\Delta S^{\circ}(\text{A}\cdot)$
-CH ₂ [•]	alkyl	33.9	-1.0	-C(O)O [•]		-2.6	10.0
>C [•]	alkyl	38.0	15.1	-C(O)NH [•]		4.1	10.0
-O [•]	alkoxy radical	8.0	-1.9	-O-O [•]	peroxy	7.5	0.0
-C [•] (O)		5.0	-10.0				

The estimation of the free enthalpy of formation using the data from Tables 2.2.8 to 2.2.10 leads to values for the gaseous state of the molecule (in some instances hypothetical state). However, few compounds and no polymers are in gas phase. For this reason, correction must be made to the gaseous state of a compound in order to estimate the free enthalpy for a specific reaction involving compounds in liquid or solid (crystalline or amorphous) state. A number of empirical rules are available for the change from gas phase to a condensed phase, and a selection of such corrections is given in Table 2.2.11 [35].

TABLE 2.2.11. Corrections to the heats of formation and entropies for change from gas phase in a condensed phase.

Phase of reagents	Phase of products	ΔH° (kcal/mol) correction	ΔS° (cal/T/mol) correction
gas	solid amorphous	-1.67	3.59
gas	solid crystalline	-4.06	9.56
liquid	solid amorphous	0.00	-9.56
liquid	solid crystalline	1.91	-7.17
solid crystalline	solid crystalline	0.00	-9.56

Using again the example of acrylonitrile polymerization, the results of the calculations using the concept of additivity of enthalpy and entropy lead to the results shown in Table 2.2.12.

TABLE 2.2.12. *Calculated heats of formation and entropies for acrylonitrile and polyacrylonitrile using the additivity model.*

Compound/reaction *	ΔH kcal/mol	ΔS cal/T/mol	Temp. °C
monomer (calc.)	41.69	9.44	25
monomer (exp.)	43.16	14.5	25
polymer (g) (calc.)	19.5	46.25	25
reaction (gg) (calc.)	-22.19	36.81	25
reaction (la) (calc.)	-22.19	27.25	25
reaction (la) (exp.)	-18.28		74.5

* g = gas, gg = gas/gas, la = liquid/solid amorphous

The agreement with the experimental value for ΔH is quite good and very close to the calculated value using molecular orbital modeling. The additivity model predicts, however, a different entropy of reaction.

Another procedure based only in part on the additivity properties of the values for ΔH^0 and ΔS^0 is based on correlation equations for a series of homolog compounds or of compounds containing a repetitive unit (such as polymers). Since the compounds in a homolog series differ by the same fragment, it can be expected that the values in a series is linear. The data used for generating the correlation equation can be either experimental or calculated values of a thermodynamic parameter. As an example, a set of experimental and calculated values for the heats of formation ΔH_f^0 for the series of saturated normal hydrocarbons C_nH_{2n+2} are plotted as a function of carbon number in Figure 2.2.4.

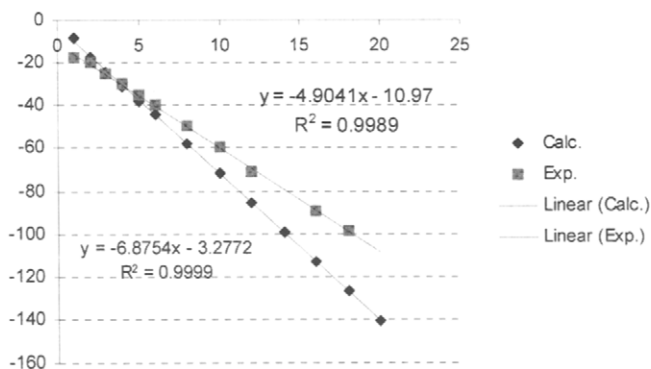


FIGURE 2.2.4. *Experimental and calculated values for the heats of formation ΔH_f^0 for the series of saturated normal hydrocarbons C_nH_{2n+2} plotted as a function of carbon number.*

The regression equation can be used for the calculation of $\Delta H_f^0(C_nH_{2n+2})$ for arbitrary values of n using a correlation equation (see also rel. 2.2.30). The results shown in

Figure 2.2.4 also put in evidence the agreement (or lack of agreement) between experimental values and the values calculated using a semiempirical MO type calculation, MOPAC-7 with AM1 parameterization [22]. A similar plot can be generated for ΔS_f^0 values. For the same series of hydrocarbons, the plot for ΔS_f^0 values is given in Figure 2.2.5.

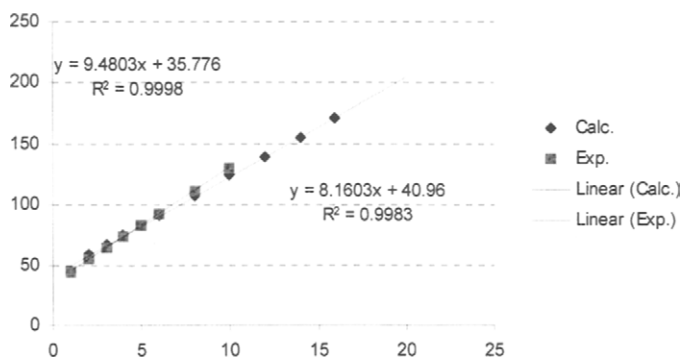


FIGURE 2.2.5. Experimental and calculated values for the entropies of formation ΔS_f^0 for the series of saturated normal hydrocarbons C_nH_{2n+2} plotted as a function of carbon number.

The regression equation has been used as rel. (2.2.32) for predicting ΔS_f^0 values for any normal saturated hydrocarbon with n carbons. The agreement between the experimental values and those calculated using MOPAC-7 MO calculation package (with AM1 parameterization) is better than the agreement for ΔH_f^0 values.

Similar correlation equations can be established for other compounds, including free radicals. Since fewer experimental data are available for free radicals or for a series of less common compounds, calculated values can be very helpful for obtaining correlation equations for ΔH_f^0 and ΔS_f^0 values (in the case of free radicals open shell MO calculations are necessary). Since many thermodynamic values for chemical reactions are calculated as the difference between the parameters for the forward reaction and those for the reverse reaction (see e.g. rel. 2.2.34), the errors between calculated and experimental thermodynamic parameters may be in part compensated such that the final calculated results are in good agreement with the experiment. However, the compensation may depend on the parameterization of the calculation procedure. For example, the calculated and experimental data for ΔH_f^0 for the series of normal 1-olefins C_nH_{2n} are plotted as a function of carbon number in Figure 2.2.6. The calculation has been done using MOPAC-7 MO calculation package [22]

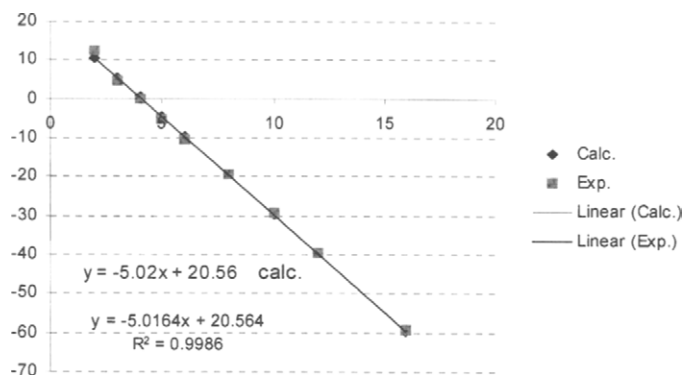


FIGURE 2.2.6. Experimental and calculated values for the heats of formation ΔH_f^0 for the series of 1-olefins C_nH_{2n} plotted as a function of carbon number.

As seen from Figure 2.2.6, the agreement between experimental and calculated data is excellent in this case, but the results do not compensate for the differences seen for the saturated series.

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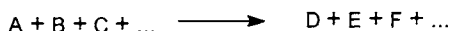
2.3 KINETIC FACTORS IN POLYMER FORMATION AND DECOMPOSITION

- General aspects

The *reaction rate* of a chemical process where A is a reactant and B is a product is defined as the variation of the concentration of A or of B versus time. The reaction rate can be expressed by the relation:

$$-\frac{d[A]}{dt} = \frac{d[B]}{dt} \quad (2.3.1)$$

where [A] and [B] are the (molar) concentrations at any time during the reaction. If in a chemical reaction of the type:



the rate of reaction depends linearly on the concentration of one reactant A, then:

$$-\frac{d[A]}{dt} = k[A] \quad (2.3.2)$$

This type of reaction is of the first order. The constant *k* is the *rate constant*. Concentrations are commonly expressed in mol/L, and *k* is expressed in s⁻¹. The rate constant *k* is temperature dependent and it is a constant only in isothermal conditions.

It is possible that the rate of reaction depends on the concentrations of the A and B species simultaneously. In this case the dependence is given by expression:

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A][B] \quad (2.3.3)$$

and the reaction is of the second order. The reaction rate constant k for second order kinetics is expressed in $\text{mol}^{-1} \text{s}^{-1}$ (different units from those used for the constant of first order kinetics).

Some chemical reactions have a reaction rate of the form:

$$-\frac{d[A]}{dt} = k[A]^n \quad (2.3.4)$$

where n is the reaction order. The value of n can be an integer, or for certain chemical reactions it can be a fractional number.

In order to understand how the constant k depends on temperature, it was assumed that the chemical reactions could take place only when the molecules collide. Following this collision, an intermediate state called an activated complex is formed. The reaction rate will depend on the difference between the energy of the reactants and the energy of the activated complex. This energy E^\ddagger is called activation energy (other notation E^a). The reaction rate also will depend on the frequency of collisions. Based on these assumptions, it was shown (e.g. [1]) that k has the following expression (Arrhenius reaction rate equation):

$$k = A \exp\left(-\frac{E^\ddagger}{RT}\right) \quad (2.3.5)$$

where A is a parameter related to the collision number, and it is called *frequency factor*. Rel. (2.3.5) indicates the explicit dependence of the rate constant k on temperature (expressed in $^\circ\text{K}$). However, both A and E^\ddagger are not strictly temperature independent, and some variation with temperature of these parameters has been studied [2].

- Kinetic characterization of step-reaction polymerization

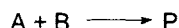
The kinetic parameters of a polymerization reaction can be correlated with the average degree of polymerization. For a polymerization reaction starting with N_0 molecules of monomer and having N molecules at a certain point during the reaction, the conversion p for the step-reaction can be defined as the ratio between the number $N_0 - N$ of molecules that reacted and the initial number of monomer molecules N_0 :

$$p = \frac{N_0 - N}{N_0} \quad (2.3.6)$$

From rel. (2.3.6) the expression of N can be obtained as $N = N_0(1 - p)$, and the average degree of polymerization \overline{DP} given by rel. (1.1.1) can be written as follows:

$$\overline{DP} = \frac{1}{1 - p} \quad (2.3.7)$$

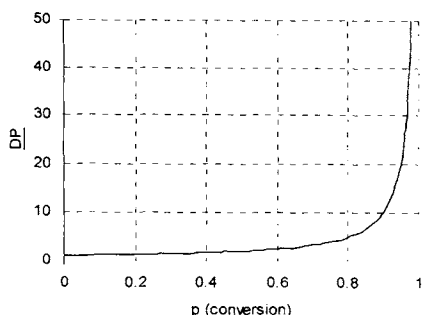
Rel. (2.3.7) shows that for step reactions DP increases slowly even at high levels of conversion p . This is illustrated in Figure 2.3.1, which gives the variation of DP as a function of p . The DP values can be related to the kinetics of the polymerization reaction, taking as an example a reaction of the form:



Assuming that this reaction is governed by a second order reaction rate, it can be written:

$$-\frac{d[A]}{dt} = k[A][B] \quad (2.3.8)$$

FIGURE 2.3.1. Variation of DP with p for a step-reaction polymerization.



In rel. (2.3.8) it can be assumed that $[A] = [B]$, which is typically used in practice to achieve high molecular weight of the polymer. Therefore, $[A][B] = [A]^2$ and the relation (2.3.8) can be integrated leading to:

$$\frac{1}{[A]} - \frac{1}{[A_0]} = kt \quad (2.3.9)$$

where $[A_0]$ is the initial molar concentration of the monomer. Since the number of molecules is proportional with the molar concentration, from rel. (2.3.6) it can be noticed that $p = ([A_0] - [A]) / [A_0]$, which is equivalent to $[A] = [A_0] (1 - p)$. Introducing this expression in rel. (2.3.9), it can be written:

$$\frac{1}{[A_0](1-p)} - \frac{1}{[A_0]} = kt \quad (2.3.10)$$

Replacing in the above expression $1/(1-p)$ with DP, the expression can be rearranged in the form:

$$DP = [A_0] kt + 1 \quad (2.3.11)$$

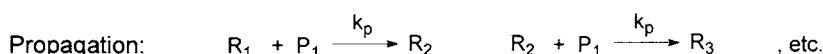
Rel. (2.3.11) correlates the value for DP with the initial monomer concentration, rate constant k and the time of reaction t . Similar theory can be developed for reactions that are of first order in one reactant and of second order in the other reactant (such as for the case of uncatalyzed polyesterification reactions).

- Kinetic characterization of free radical polymerization

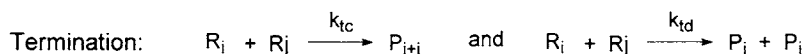
A significant number of chain reaction polymerizations have a free radical mechanism. In this case the polymerization starts with an initiator I_0 that yields free radicals in a reaction controlled by the reaction rate k_d and forms free radicals R_0 . The free radical R_0 reacts with a monomer P_1 in a reaction with the rate constant k_i and forms a new free radical R_1 . These two processes form the initiation step of the polymerization, and they can be written as follows:



The process is propagated by reactions of the type:



For the propagation reaction it can be approximated that all reaction rates k_p are equal. The termination can be done as previously indicated by two processes, radical coupling and disproportionation. These reactions are characterized by specific reaction rates k_{tc} and k_{td} as shown below:



The reaction of a radical with a monomer P_1 is typically a fast reaction, such that the rate-determining step is the formation of free radicals from the initiator I_0 . The total concentration of radicals $[R]$ satisfies, therefore, an expression of the form:

$$\frac{d[R]}{dt} = -2fk_d[I_0] \quad (2.3.12)$$

where f is the "initiator efficiency" defined as the ratio of the number of radicals that initiate a polymer chain and the number of radicals formed from the initiator (not all radicals are able to initiate the polymerization).

The radicals disappear because of the termination reaction with a rate given by the expression:

$$\frac{d[R]}{dt} = -2k_t[R]^2 \quad (2.3.13)$$

where $k_t = k_{tc}$ or k_{td} . Assuming that the formation and disappearance of radicals occur at the same rate (steady state assumption), from rel. (2.3.12) and (2.3.13) results:

$$2 f k_d [I_0] = 2 k_t [R]^2 \quad (2.3.14)$$

The rate for the propagation of polymerization is given by the expression:

$$\frac{d[P_1]}{dt} = -k_p [P_1][R] \quad (2.3.15)$$

By obtaining the expression of $[R]$ from rel. (2.3.14) and including it in rel. (2.3.15), the rate of polymerization is obtained in the form:

$$\frac{d[P_1]}{dt} = -k_p [P_1] \sqrt{\frac{fk_d[I_0]}{k_t}} \quad (2.3.16)$$

This expression shows the parameters determining the rate of polymerization, namely the kinetic constants k_p , k_d and k_t the concentration of the monomer $[P_1]$ and that of the initiator $[I_0]$.

The ratio of the rate of polymerization and the rate of initiation is an important parameter in chain polymerization reactions and is known as *average kinetic chain length* $\bar{\nu}$. This parameter gives the average number of monomer units per chain initiated. Using rel. (2.3.17) and (2.3.12) the expression for $\bar{\nu}$ can be obtained in the form:

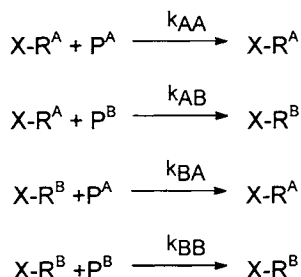
$$\bar{\nu} = \frac{d[P_1]}{dt} / \frac{d[R]}{dt} = \frac{k_p [P_1]}{2(fk_d k_t [I_0])^{1/2}} \quad (2.3.17)$$

In the absence of side reactions and when the termination reaction occurs by disproportionation, $DP = \bar{\nu}$. In the case that termination takes place by a radical coupling reaction, then $DP = 2\bar{\nu}$.

The previous description of the kinetics of polymerization is only the ideal case for many practical applications. Various deviations from the models are encountered in practice.

- Kinetic aspects of copolymer formation

The composition of copolymers obtained in a free radical polymerization can be predicted based on several kinetic parameters of copolymerization reaction. For a copolymer starting with two species of monomer P^A and P^B , it can be assumed that the rate of addition of the monomer to a growing free radical depends only on the nature of the end group. If the chain is indicated by X , this is equivalent with the assumption that the radical R_1^A will act equivalently with $X-R^A$, and the radical R^B will act equivalently with $X-R_1^B$. The following reactions will take place in the system:



where k_{AA} , k_{AB} , k_{BA} and k_{BB} are the rate constants. Assuming that these reactions are of second order and that the rate of conversion of $X-R^A$ into $X-R^B$ is equal with the rate of conversion of $X-R^B$ into $X-R^A$, the following relation is true:

$$k_{BA} [X-R^B] [P^A] = k_{AB} [X-R^A] [P^B] \quad (2.3.18)$$

In this case, the rate of disappearance of the monomers P^A and P^B is described by the expressions:

$$-\frac{d[P^A]}{dt} = k_{AA} [X-R^A] [P^A] + k_{BA} [X-R^B] [P^A] \quad (2.3.19a)$$

and

$$-\frac{d[P^B]}{dt} = k_{AB} [X-R^A] [P^B] + k_{BB} [X-R^B] [P^B] \quad (2.3.19b)$$

By defining $r_A = k_{AA}/k_{AB}$ and $r_B = k_{BB}/k_{BA}$ and combining rel. (2.3.19a) and (2.3.19b), it results that the composition of a copolymer formed at any instant is given by an expression known as copolymer equation, which has the form:

$$\frac{d[P^A]}{d[P^B]} = \frac{[P^A](r_A [P^A] + [P^B])}{[P^B]([P^A] + r_B [P^B])} \quad (2.3.20)$$

The parameters r_A and r_B are known as *monomer reactivity ratios* representing the ratio of rate constants for a radical to add to its own type polymer vs. rate constants for a radical to add to the other type polymer. When $k_{AA} = 0$ and $k_{BB} = 0$, it can be seen that $r_A = 0$, $r_B = 0$, and each radical reacts exclusively with the other monomer. Rel. (2.3.20) is then reduced to $d[P^A]/d[P^B] = 1$, and the monomers alternate regularly along the chain of the copolymer, regardless of the composition of the monomer feed (an excess of one monomer may remain unreacted). This is an ideal case, but copolymers such as that made from (a) styrene and (b) diethyl fumarate ($r_A = 0.3$, $r_B = 0.07$) can be close to the ideal case. The styrene/diethyl fumarate polymerization has the tendency to lead to an azeotropic copolymer with 57 mole percent styrene, regardless the feed composition. When the initial composition of the monomers is different from 57 mole percent, the *alt*-copolymer is formed until one of the materials is finished and the remaining monomer forms a homopolymer.

For the case that the two radicals show identical preference for adding any of the two monomers, then $r_A = 1/r_B$ and rel. (2.3.20) becomes $d[P^A]/d[P^B] = r_A [P^A]/[P^B]$. The composition of the copolymer depends in this case only on the composition of the monomer feed. This case is an ideal one, and in reality for many polymers $0 < r_A r_B < 1$ with a polymer composition depending on both composition of the monomer feed and particular reaction rates (radical reactivities) of the two species. One additional case is that with both $r_A > 1$ and $r_B > 1$ when the formation of block polymers is favored.

Rel. (2.3.20) allows the determination at any time during the reaction of the instantaneous composition of the feed and of the copolymer. Using the notation F_A for the mole fraction for monomer "A" in the polymer and F_B for the other monomer ($F_B = 1 - F_A$), and the notation f_A for monomer "A" in the feed and f_B for the other monomer, ($f_B = 1 - f_A$), the following expressions can be written:

$$F_A = \frac{d[P^A]}{d[P^A] + d[P^B]} \quad (2.3.21a)$$

$$f_A = \frac{[P^A]}{[P^A] + [P^B]} \quad (2.3.21b)$$

With these notations and using rel. (2.3.20), the expression of F_A takes the form:

$$F_A = \frac{r_A f_A^2 + f_A f_B}{r_A f_A^2 + 2f_A f_B + r_B f_B^2} = \frac{r_A z^2 + z}{r_A z^2 + 2z + r_B} \quad (2.3.22)$$

where

$$z = f_A/f_B = [P^A]/[P^B] \quad (2.3.23)$$

Rel. (2.3.22) describes the instantaneous composition of the polymer as a function of constants r_A , r_B and the feed composition. The variation of copolymer composition F_A as a function of the feed composition f_A for a binary mixture is shown in Figure 2.3.2 for several r_A and r_B values.

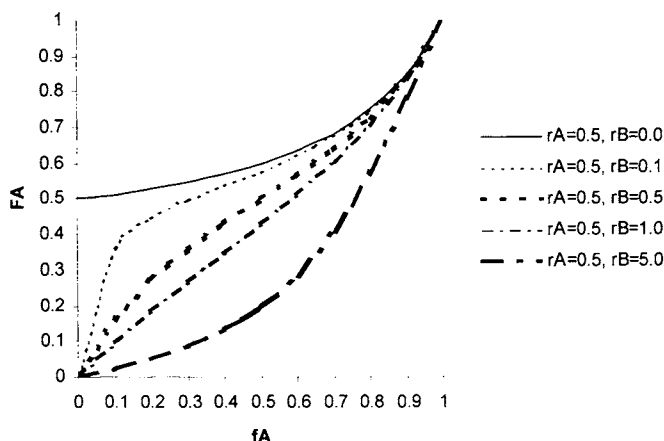


FIGURE 2.3.2. Variation of copolymer composition F_A as a function of the feed composition f_A for a binary mixture and for several r_A and r_B values.

As seen from Figure 2.3.2, the composition of the polymer and that of the feed is usually different. As the reaction progresses, only by maintaining a constant composition of the feed is it possible to obtain a uniform copolymer. For r_A and r_B less than unity, the variation of F_A as a function of f_A has a point where $(F_A)_c = (f_A)_c$, where the composition of the copolymer is identical to the concentration of the feed. The copolymerization at this concentration is known as azeotropic copolymerization. This is achieved when f_A has the value given by rel. (2.3.24):

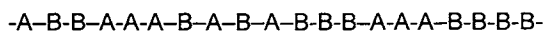
$$(f_A)_c = \frac{1 - r_A}{2 - r_A - r_B} \quad (2.3.24)$$

Rel. (2.3.24) can be easily obtained by substituting $F_A = f_A$ in rel. (2.3.22).

The information on polymer composition does not provide any information regarding the overall rate of copolymerization. This depends on the rates of initiation and termination (for details see e.g. [3]).

- The characterization of sequence distribution in copolymers

An important copolymer characteristic is the monomer unit arrangement in the polymeric chain. The monomer units in a copolymer are present in sequences of monomers or blocks of the same nature, and these sequences can be formed from one monomer, two, three, or from many monomer units. There are two related parameters that characterize this arrangement, namely the "run number" and the "number average sequence length" or N.A.S.L. The *run number* R is defined as the average number of sequences (blocks) occurring in a copolymer per 100 monomer units (the end groups are included) [4]. As an example, a fragment of 20 monomer units (instead of 100 as in the definition) is shown below, with the blocks underlined:



In this example (of only 20 monomers), there are 10 blocks, and therefore $R = (10/20) \cdot 100 = 50\%$. The value of R can be written in the form:

$$R = 100 \frac{\text{Number of blocks}}{\text{Number of monomers}} \quad (2.3.25)$$

The run number R is related to the number of A-B bonds in the copolymer, and since there are as many A runs as B runs, it can be seen that the % of A-B bonds is given by the expression:

$$\% \text{A-B bonds} = R/2 \quad (2.3.26a)$$

The number of B units that have a B neighbor on the right (or left) is equal to the total number of B monomer units minus those that have an A neighbor. Therefore, the % of B-B bonds is given by:

$$\% \text{B-B bonds} = 100 F_B - R/2 \quad (2.3.26b)$$

and similarly:

$$\% \text{A-A bonds} = 100 F_A - R/2 \quad (2.3.26c)$$

where $100 F_A$ and $100 F_B$ are the molar percentages of monomer units (A and respectively B) present in the copolymer.

The percentages of A-A, B-B, and A-B bonds are related to the probability π that a given B monomer unit has an A unit on its right (or left). This probability is given by the expression:

$$\pi_{BA} = \pi_{AB} = \frac{R/2}{100F_B} = \frac{R}{200F_B} \quad (2.3.27)$$

Similarly, the probability of A-A bonds in the copolymer is given by:

$$\pi_{AA} = \frac{(100F_A - R/2)}{100F_A} \quad (2.3.28)$$

and an analogous relation is valid for π_{BB} . These probabilities can be further utilized, for example to determine the probability that a B unit has A units on both sides. In this case $\pi_{ABA} = (\pi_{AB})^2$. The knowledge of copolymer composition and of R allows the calculation of the probability of any structural arrangement in the polymer.

The run number R can be calculated in a copolymer based on the feed composition and monomer reactivity ratios r_a and r_b . For this purpose, the rate at which the monomer units are incorporated into the polymer is written in the form:

$$\frac{d([P^A] + [P^B])}{dt} = k_{AA}[X-R^A][P^A] + k_{AB}[X-R^A][P^B] + k_{BA}[X-R^B][P^A] + k_{BB}[X-R^B][P^B] \quad (2.3.29)$$

The rate at which runs (sequences) are generated in the copolymer is given by the expression:

$$\frac{dS}{dt} = k_{AB}[X-R^A][P^B] + k_{BA}[X-R^B][P^A] \quad (2.3.30)$$

The ratio of rel. (2.3.29) and (2.3.30), with the utilization of rel. (2.3.18), (2.3.23) and of the expressions for r_A and r_B , leads to the formula:

$$\frac{d([P^A] + [P^B])}{dS} = 1 + \frac{r_A}{2}z + \frac{r_B}{2z} \quad (2.3.31)$$

However, it can be seen that the definition of R is equivalent with the expression:

$$R = 100 \frac{dS}{d([P^A] + [P^B])} \quad (2.3.32)$$

which leads to the formula:

$$R = \frac{200z}{r_A z^2 + 2z + r_B} \quad (2.3.33a)$$

Rel. (2.3.33a) allows the calculation of the run number R based on the feed composition and the monomer reactivity ratios. The run number R expressed per 100 monomer units can be replaced with a fraction run number R_f given by the formula:

$$R_f = \frac{2z}{r_A z^2 + 2z + r_B} \quad (2.3.33b)$$

This number can be determined from experimental data, including from pyrolysis data (see Section 4.2).

Related to the run number R is the *number average sequence length* (N.A.S.L.), which is defined for a monomer A in an AB copolymer as the total number of A monomers in the polymer chain divided by the total number of blocks of monomer A (regardless the block length) [5]. Using the notation $n(A)$ for N.A.S.L., the expression for $n(A)$ is the following:

$$n(A) = \frac{\text{Total number of A}}{\text{Total blocks of A}} \quad (2.3.34)$$

Both the run number R and the number average sequence length can be obtained from pyrolysis data.

- Kinetic factors in pyrolytic reactions

For pyrolytic reactions, the variation of the molar concentration $[A]$ of a substance during the pyrolysis is not always the most appropriate parameter to be monitored. The calculation of $[A]$ can be a problem for many types of samples, and very frequently during pyrolysis not only one decomposition process takes place. In this case, the overall reaction kinetics must be considered. A more convenient parameter for monitoring pyrolytic reactions is, for example, the sample weight. For a reaction of the first order, by multiplying rel. (2.3.2) with the volume V and the molecular weight M of the substance A, since $W = [A] V M$, the following expression is obtained:

$$-\frac{dW}{dt} = k W \quad (2.3.35a)$$

where W is the weight (mass) of the sample at any time during the reaction. This type of equation can approximate (with good results) the kinetics for many pyrolytic processes. Rel. (2.3.35a) can be easily integrated to give:

$$\ln W \Big|_{t=0}^t = -k t \quad \text{or} \quad \ln \frac{W}{W_0} = -k t \quad \text{or} \quad \frac{W}{W_0} = \exp(-k t) \quad (2.3.35b)$$

where W_0 is the initial sample weight (at $t = 0$).

In some cases, the pyrolysis leaves a residue of undecomposed sample of the weight W_f (final weight). In this case rel. (2.3.35a) will be

$$-\frac{dW}{dt} = k(W - W_f) \quad (2.3.36)$$

This type of relation can be applied to pyrolytic processes even if the reaction is not of the first order. In this case the reaction rate is described by the relation:

$$-\frac{dW}{dt} = k(W - W_f)^n \quad (2.3.37)$$

and the reaction order n is not necessarily an integer. Relations of the type (2.3.35a), (2.3.35b) or (2.3.36), which were used for weight, can be applied for other parameters. Examples of such parameters are the residual mass fraction (W/W_0), the volatilized mass fraction $\alpha = (1 - W/W_0)$ also known as conversion and equal to the ratio of the volatilized mass to the initial mass, and for uniform polymers the number of polymer molecules.

When the pyrolytic process does not occur in gas phase, different problems appear. Although equations of the type (2.3.35a) can be used in certain cases, these may lead to incorrect results. Various empirical models were developed for describing the reaction kinetics during the pyrolysis of solid samples [6]. Most of these models attempt to establish equations that will globally describe the kinetics of the process and fit the pyrolysis data.

The temperature dependence of the rate of reactions is particularly important for the pyrolytic processes. Rel. (2.3.5) and (2.3.35a) can be used for the understanding of the common choices for the pyrolysis parameters, their combination leading to:

$$-\frac{dW}{dt} = A \exp\left(-\frac{E^\#}{RT}\right) W \quad (2.3.38)$$

Knowing the values for the frequency factor A , activation energy $E^\#$ and temperature T , this equation can be integrated and provide the value of weight loss at a certain temperature. An example of the use of rel. (2.3.38) to monitor the weight loss as a function of temperature is given in Section 3.1. The values for the activation energies can be obtained from thermogravimetric studies. Using the notations T_f and T_i for the final and initial temperature in a thermogram, T_s for the temperature of inflection in the TG curve (typically obtained from the derivative curve DTG), and ω for the fraction of polymer degraded at temperature T (estimated from the volatilized mass fraction), the activation energy for the major step in the thermogram can be determined from the expression [7]:

$$\ln[-\ln(1 - \omega)] = (E^\#/RT_i^2)(100/T_f - T_i)(T - T_s) + C \quad (2.3.39)$$

where C is a constant that can be obtained from the plot of $\ln[-\ln(1 - \omega)]$ versus $(T - T_s)$.

The calculation of the frequency factor A can be done using the expression [8]:

$$A = \beta E^{\#} \exp(E^{\#}/R T) / R T_{\max}^2 \quad (2.3.40)$$

where β is the heating rate and T_{\max} is the temperature at which the rate of degradation is maximum.

Some activation energies and the decomposition rate at 350° C for several common polymers are given in Table 2.3.1 [9–14].

TABLE 2.3.1. *Activation energy and rate at 350° C for several common polymers.*

Polymer	Activation energy $E^{\#}$ kcal/mol	Frequency factor A s ⁻¹	Rate at 350° C weight %/min.
poly(methyl methacrylate)	32-55	$1.5 \cdot 10^8$	5.2 - 200
poly(methyl acrylate)	37	$1.6 \cdot 10^{10}$	10
poly(α -methylstyrene)	58-65	$8.5 \cdot 10^{18}$	228
poly(<i>m</i> -methylstyrene)	59	$7.5 \cdot 10^{16}$	0.9
polystyrene	45	$2.4 \cdot 10^{11}$	0.235
poly(isobutylene)	52	$7 \cdot 10^{14}$	2.4
polypropylene	59	$5.75 \cdot 10^{15}$	0.069
polyethylene (linear)	65	$4.3 \cdot 10^{16}$	0.004
polyethylene (branched)	70	$4.8 \cdot 10^{18}$	0.008
poly(vinylcyclohexane)	52	$1.3 \cdot 10^{14}$	0.450
polytetrafluoroethylene	80	$3.9 \cdot 10^{18}$	$2 \cdot 10^{-6}$
poly(trifluorostyrene)	67	$1.3 \cdot 10^{20}$	2.4
poly(trifluorochloroethylene)	50	$1.2 \cdot 10^{13}$	0.2
poly(trifluoroethylene)	53	$1.3 \cdot 10^{13}$	0.02
poly(vinylidene fluoride)	48	$2.3 \cdot 10^{11}$	0.02
poly(<i>p</i> -xylylene)	76	$1.5 \cdot 10^{20}$	0.002
polybenzyl	53	$3.9 \cdot 10^{12}$	0.006
poly(<i>N-p</i> -chlorophenylmaleimide)	52	$7.6 \cdot 10^8$	$2.9 \cdot 10^{-6}$
poly(<i>N</i> -phenylmaleimide)	45	$7.2 \cdot 10^{16}$	$3.5 \cdot 10^4$
poly(<i>N-p</i> -nitrophenylmaleimide)	33	$1.5 \cdot 10^{12}$	$2.4 \cdot 10^4$

Besides the reaction rate k , which provides a description of how fast a certain process takes place at a given temperature, some "integral" parameters (within a time range) were defined for the same purpose. One such parameter is the half decomposition time $t_{1/2}$, which is the time required to get $W/W_0 = 1/2$. Making the approximation that k does not vary with the heating time, the formula for $t_{1/2}$ calculated from rel. (2.3.38) is the following:

$$t_{1/2} = (\log 2) / k \quad (2.3.41)$$

The required approximations for the validity of equation (2.3.41) are rather difficult to meet in practice.

- Models for the kinetics of the pyrolytic processes of solid samples

The kinetics equation of the type described by rel. (2.3.35a) is commonly applied for describing the overall reaction kinetics during pyrolysis. However, this equation provides only an approximation when the process is not composed of a single reaction [15]. The pyrolysis of solid samples is usually a complicated process, and rel. (2.3.35a) may lead to erroneous results. The simpler relations valid for the kinetics in

homogeneous systems do not fit well the experimental data for solid samples. Factors related to heterogeneous reactions must be taken into account in this case. A series of models have been developed for a better description of the process and can be found in the dedicated literature (see e.g. [16–18]).

A more empirical approach [19] for describing the kinetics of the pyrolytic reactions in solid state is to use a parametric equation that includes formulas for all possible categories of kinetics mechanisms known to occur for the chemical reactions of solid samples. Considering $F = W/W_0$ the mass fraction of the unreacted substance at the time t , the empirical kinetics equation for heterogeneous systems can be expressed in the general form:

$$\frac{dF}{dt} = -k f(F) \quad (2.3.42)$$

where k is a constant and $f(F)$ is a function that can be chosen of the form:

$$f(F) = F^m (1 - F)^n [-\ln(1 - F)]^p \quad (2.3.43)$$

The terms in rel. (2.3.43) attempt to describe the reaction rate controlled by the movement of the phase boundary, diffusion, nucleation in solid state, etc., and different values (including zero values) for m , n and p were proposed in literature (see e.g. [20]). Different combinations of m , n , and p values were found suitable for describing different dominating processes. Table 2.3.1 indicates some common values for m , n and p used in equation (2.3.43).

TABLE 2.3.1. Common values from literature [19] for m , n and p in equation (2.3.43).

m	n	p	Type of process
0	0	0	Phase boundary reaction
0	1/2 2/3	0	Phase boundary reaction
0	1	0	Unimolecular decay
$m < 1, 3/4$	0	0	Nucleation
1	0	0	Linear growth of nuclei
-1	0	0	Diffusion
0	0	-1	Diffusion
$0.5 < m < 1$	$0.5 < n < 1$	0	Nucleation
$m > 1$	$n < 1$	0	Linear growth of nuclei
0	1	1/2, 2/3, 3/4	Growth of nuclei
0	0	-1	Diffusion
m	n	p	Any complicated case

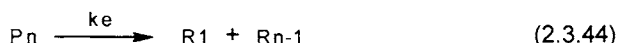
For the reactions in solid state, several other empirical equations as well as numerical methods were proposed [21] to better simulate the dependence on temperature of the reaction rate (see e.g. [16]).

- Pyrolysis kinetics for uniform repetitive polymers with a volatile monomer

Thermal decomposition of uniform repetitive polymers was extensively studied in literature [22–24] in relation to the thermal stability of synthetic polymers. An equation for the kinetics of decomposition has been developed based on the study of the steps occurring during pyrolysis involving a free radical chain mechanism [22]. This theory gives good agreement for highly repetitive polymers but does not provide appropriate kinetics equations for non-repetitive polymers or for polymers with more complex decomposition pathways.

The pyrolytic process of a repetitive polymer frequently takes place with the formation of small volatile molecules and has a polymeric chain scission mechanism, as described in Section 2.1. However, the theory developed below considers only the monomer as being volatile and does not take into consideration that other small molecules may leave the pyrolysis system (this case is sometimes indicated as a closed system).

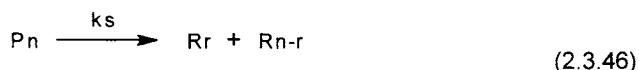
Taking a polymer with a degree of polymerization (DP) equal to n , the end scission reaction can be described by the chemical equation:



where P_n is the molecule of the polymer, R_1 is the radical with one monomeric unit, R_{n-1} is the radical with $n-1$ monomeric units, and the kinetic constant k_e governs the end scission reaction. Using the notation P_n for both the molecule itself and also for the number of molecules of polymer with $DP = n$, the kinetics of the reaction can be described by the equation:

$$\frac{dP_n}{dt} = -k_e P_n \quad (2.3.45)$$

where a first order reaction kinetics is assumed. This relation is similar to equation (2.3.1) where the concentration is replaced by the number of molecules. The kinetic constant k_e governs the end scission. For most polymers the end scission reaction (unzipping) plays a more important role compared to any individual random scission (see Section 2.1). However, random scission reactions with formation of radicals also should be considered. These are described by reactions of the type:



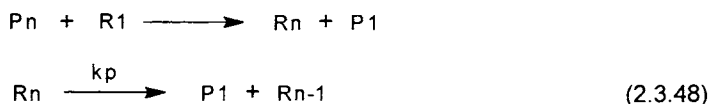
and the kinetic constant k_s governs the random scission. The kinetics equation obtained by considering all reactions (2.3.46), with $r = 2, 3, 4, \dots$ will be given by the expression:

$$\frac{dP_n}{dt} = -k_s (n-1) P_n \quad (2.3.47)$$

where the assumption was made that k_s remains constant for all r values. It also should be noted that in the chemical reactions (2.3.43) and (2.3.46) only the macromolecules

with the $DP = n$ were considered, but the polymer does not consist of molecules with only one degree of polymerization. This fact will be considered later.

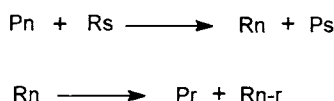
After the radical formation, intermolecular chain transfer reactions take place. A special case of chain transfer is the propagation reaction (see Section 2.1) of the type:



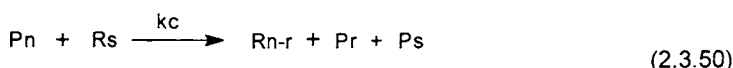
The kinetics of radical R_n disappearance will be expressed by the equation:

$$\frac{dR_n}{dt} = -k_p R_n \quad (2.3.49)$$

This transfer reaction with the formation of the monomer P_1 is governed by the propagation rate constant k_p and is more common than other reactions for many polymers. More general types of chain transfer reactions followed by radical decompositions can be written as follows:



The sum of the two previous reactions gives the following result:



This type of transfer reaction is governed by a different kinetic constant k_c , which again is assumed the same for all $r = 2, 3, 4, \dots$. The kinetics equation for all propagation and chain transfer reactions can be written as follows:

$$\frac{dP_n}{dt} = -k_c (R/V)(n-1)P_n + k_c (R/V) \sum_{j=n+1}^N P_j + k_c (R_n/V) \sum_{i=L}^N P_i \quad (2.3.51)$$

where the first term accounts for the rate of disappearance of P_n by transfer type initiation, the middle term accounts for the formation of P_r , and the last term accounts for the formation of P_s by termination of a radical by transfer. In equation (2.3.51), R is the total number of radicals, V is the sample volume, and R_n is the number of radicals with $DP = n$. Also, in equation (2.3.51) L is the degree of polymerization of the smallest non-volatile molecule, and N is the maximum degree of polymerization in the sample.

The polymeric chain scission mechanism is terminated by one or more of the following types of termination reaction:

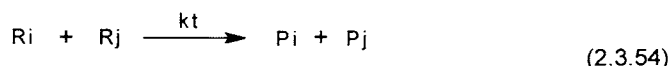
- First order termination (due to disproportionation, etc.) of the form:



with the kinetics described by the equation:

$$\frac{dP_n}{dt} = k_t R_n \quad (2.3.53)$$

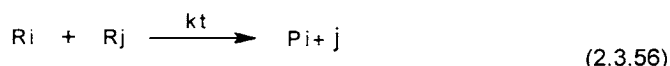
- Second order disproportionation:



with the kinetics described by the equation:

$$\frac{dP_n}{dt} = k_t (R/V) R_n \quad (2.3.55)$$

- Second order recombination:



with the kinetics described by the equation:

$$\frac{dP_n}{dt} = k_t \frac{1}{2} \sum_{i+j=n}^N (R_i R_j / V) \quad (2.3.57)$$

The rate constant for the termination reactions are all noted with k_t , but depending on the type of termination, different k_t values will be used.

The total rate of change in the number of macromolecules with the DP = n can be expressed by adding equation (2.3.45) for end scission, (2.3.47) for random scission, and (2.3.51) for transfer reactions and one of the equations (2.3.53), (2.3.55), or (2.3.57) for the termination. The result can be simplified by using the formula:

$$k_c (R_n / V) \sum_{n=i}^N n P_n = k_c R_n (do / M) \quad (2.3.58)$$

where "do" is the density of the sample and M is the molecular weight of a monomeric unit. The final formula, which gives the kinetics of the decomposition of molecules P_n , will be the following:

$$\frac{dP_n}{dt} = -k_e P_n - (n-1)[k_s + k_c (R/V)] P_n + k_c [(do/M) R_n + (R/V) \sum_{j=n+1}^N P_j] + k_t \beta R_n \quad (2.3.59)$$

In equation (2.3.59) β is the term that accounts for the termination step, and it can have the expressions:

$$\beta = 1 \quad \text{for first order disproportionation} \quad (2.3.60a)$$

$$\beta = R / V \quad \text{for second order disproportionation} \quad (2.3.60b)$$

$$\beta = \frac{1}{2 R_n} \sum_{i+j=n}^N (R_i R_j / V) \quad \text{for second order recombinations} \quad (2.3.60c)$$

Similar considerations with those described for P_n can be made for the calculation of the rate of reactions of R_n species. The rate of change of the number of radicals R_n can be described by the equation:

$$\frac{dR_n}{dt} = k_e P_{n+1} + [2k_s + k_c (R / V)] \sum_{j=n+1}^N P_j - [k_c (d_o / M) + k_p + k_t \beta] R_n + k_p R_{n+1} \quad (2.3.61)$$

The kinetics equations (2.3.59) and (2.3.61) allow the calculation of the weight loss rate for the polymer during pyrolysis. However, as previously indicated, the polymer does not consist of molecules with only one degree of polymerization. Therefore, a global kinetics equation for all the polymerization degrees $n = 2, 3, 4 \dots N$ should be obtained. For this purpose it is convenient to use the symbol M_o for the total number of polymeric molecules, where:

$$M_o = \sum_{n=2}^N P_n \quad (2.3.62)$$

and the symbol M_1 for the total number of monomeric units in the polymer sample, where:

$$M_1 = \sum_{n=2}^N n P_n \quad (2.3.63)$$

The ratio M_1/M_o is the average degree of polymerization, and it is convenient to use the following notation:

$$x = DP = M_1/M_o \quad (2.3.64)$$

The average degree of polymerization x depends on time (as M_o and M_1 depend on time) during the pyrolytic process. The initial value of x^0 (for $t = 0$) is a constant for a certain material. Using rel. (2.3.63), it is possible, using the value M for the molecular weight of the monomer, to write the formula for the weight W (in g) of the polymer:

$$W = M \sum_{n=2}^N n P_n = M M_1 \quad (2.3.65)$$

The rate loss of the weight W during pyrolysis, equivalent to formation of non-polymeric molecules, can be easily calculated from the loss of M_1 (number of monomeric units) in the polymer.

With the above notations, by taking the sum over n in equation (2.3.59) for the whole range of polymeric species ($n = 2, 3 \dots N$), the result will be given by the expression:

$$\frac{dM_0}{dt} = \frac{d \sum_{n=2}^N P_n}{dt} = -k_e M_0 - [(k_s + k_c (R/V))] M_1 + [k_c (do/M) + k_t \beta] (R - R_1) \quad (2.3.66)$$

Taking the sum over n in rel. (2.3.61) and assuming that the concentration of radicals in a steady state is constant ($dR_n/dt = 0$), the result will be given by the expression:

$$0 = [2k_s + k_c (R/V)] M_1 + 2k_e M_1/x - [k_c (do/M) + k_t \beta] R \quad (2.3.67)$$

Adding rel. (2.3.66) and (2.3.67), the result will be given by the expression:

$$\frac{dM_0}{dt} = [(k_s + k_c (R/V))] M_1 + k_e M_0 - [k_c (do/M) + k_t \beta] R_1 \quad (2.3.68)$$

where the first two terms account for the gain in molecules by initiation and transfer, and the third term accounts for the loss by termination of R_1 followed by evaporation of P_1 .

In order to find the corresponding kinetics equation for M_1 , equation (2.3.59) and (2.3.61) are multiplied by n , then the sum over all values of polymerization degrees $n = 2, 3 \dots N$, is taken, and the two expressions are added. This gives the formula:

$$\frac{dM_1}{dt} = -[k_c (do/M) + k_t \beta] R_1 - k_p (R - R_1) \quad (2.3.69)$$

The first term in equation (2.3.69) accounts for the weight loss due to termination of R_1 and the second for the weight loss due to unzipping.

The solution of rate equations (2.3.68) or (2.3.69) is not always simple. A series of particular cases, however, are easier to solve. For this purpose, several parameters describing the polymer should be introduced. One parameter defined originally for the polymerization reaction is the kinetics chain length ϵ . The kinetics chain length is defined as the average number of monomers that react with an active center from its formation until it is terminated during the polymerization process. In the same manner, for the depolymerization process, the zip length $1/\gamma$ is defined. This is the average number of monomer molecules eliminated per kinetics chain during depolymerization. Low values of $1/\gamma$ mean that little monomer is eliminated during depolymerization but not necessarily that there is little degradation. It can be shown [25] that the zip length can be defined using the relation:

$$1/\gamma = \frac{\text{probability of propagation}}{\text{probability of termination} + \text{probability of transfer}} = \frac{k_p R}{k_t \beta R + k_c (do/M) R} \quad (2.3.70a)$$

which can be written in the form:

$$1/\gamma = \frac{k_p}{k_t \beta + k_c (d_o / M)} \quad (2.3.70b)$$

The elimination of $R - R_1$ and R_1 in rel. (2.3.68) and in (2.3.69) with the aid of rel. (2.3.67) and (2.3.70b), and the combination of the two expressions gives the rate of weight loss (after multiplication with M) as a function of zip length γ by the expression:

$$\frac{dM_1}{dt} = (1 - 1/\gamma) \frac{dM_o}{dt} - [(1 + 1/\gamma) k_s + k_c (R / V)] M_1 - (1 + 1/\gamma) k_e M_o \quad (2.3.71a)$$

where the expression for dM_o/dt can be replaced after it is obtained from rel. (2.3.68). This replacement will give the expression:

$$\frac{dM_1}{dt} = -1/\gamma [2k_s + k_c (R / V)] M_1 - 2/\gamma k_e M_o - (1 - 1/\gamma) [k_c (d_o / M) + k_t \beta] R_1 \quad (2.3.71b)$$

The rate of weight loss (disappearance of monomeric units from the polymer) as a function of the degree of polymerization x is obtained from rel. (2.3.71a) by replacing dM_o/dt with $-(M_1 / x^2) dx/dt + (1 / x) dM_1/dt$ obtained from the derivatization of rel. (2.3.64). The introduction of this result in rel. (2.3.71a) leads after division with M_1 to the expression:

$$\left(\frac{1 - 1/\gamma}{x} - 1 \right) \frac{1}{M_1} \frac{dM_1}{dt} = (1 - 1/\gamma) \frac{1}{x^2} \frac{dx}{dt} + (1 + 1/\gamma) k_s + k_c (R / V) + (1 + 1/\gamma) \frac{k_e}{x} \quad (2.3.72)$$

Based on rel. (2.3.65) it can be seen that:

$$\frac{1}{M_1} \frac{dM_1}{dt} = \frac{d(\ln W)}{dt} \quad (2.3.73)$$

The behavior of a polymer during depolymerization depends very much on the initial average degree of polymerization x^0 and the ratio between x^0 and the zip length $1/\gamma$.

The solution for the equations (2.3.71b) or (2.3.72) are not obtained for the general case, but for particular types of polymer will give information regarding the decomposition kinetics.

For example, for the case of a short zip length with $1/\gamma \ll x$ and with k_e and R_1 small (unzipping does not play an important role), rel. (2.3.71b) and rel. (2.3.72) will give respectively:

$$\frac{1}{M_1} \frac{dM_1}{dt} = -1/\gamma [2k_s + k_c (R / V)] \quad \text{and} \quad \frac{1}{x^2} \frac{dx}{dt} = -[k_s + k_c (R / V)] \quad (2.3.74)$$

In this case only the value of x of the polymer decreases due to random scissions. Neglecting in rel. (2.3.74) the transfer reactions, the equation can be integrated to give $1/x = k_s t$.

For the case of k_e , k_c and R_1 small (again unzipping not playing an important role), but with a long zip $1/\gamma \gg x$, rel (2.3.68) will be reduced to:

$$\frac{dP_n}{dt} = -(n-1)k_s P_n \quad (2.3.75)$$

For an initial molecular weight distribution P_n^0 , equation (2.3.75) gives the value for P_n of the form:

$$P_n = P_n^0 \exp[-(n-1)k_s t] \quad (2.3.76)$$

For an initial monodisperse polymer $x = x^0$ and $dx/dt = 0$, which leads for rel. (2.3.72) to the form:

$$\frac{1}{M_1} \frac{dM_1}{dt} = -k_s x^0 \quad (2.3.77)$$

Other cases can be solved following similar reasoning. For example, for large k_e and short zip, rel. (2.3.72) takes the form:

$$\frac{1}{M_1} \frac{dM_1}{dt} = -(1 + 1/\gamma) \frac{k_e}{x} \quad (2.3.78)$$

The initial molecular weight distribution of the polymer is another factor determining the possibility of solving the kinetics equations. Solutions are possible when the polymer is close to a monodisperse system or when the molecular weight distribution of the polymer is known and can be described by a specific formula. A case like this is that of the "most probable" type polymer, where the distribution P_n is related to x by the formula:

$$P_n = \frac{M_1}{x^2} (1 - 1/x)^{n-1} \quad (2.3.79)$$

The average sample weight M M_1 and the average degree of polymerization P_n vary with time during depolymerization; however, due to the random nature of the process, rel. (2.3.72) is preserved.

The type of termination as indicated above (see rel. (2.3.53), (2.3.55), or (2.3.57)), may also influence the type of solution for the kinetics equations.

Based on various considerations and using rel. (2.3.73), several particular equations can be established for the number of monomer units lost during pyrolysis or for the weight loss during pyrolysis. In this way, the solutions are easier to obtain. A summary of these equations is given in Table 2.3.2 (see. e.g. [16]).

TABLE 2.3.2. A summary of equations with readily obtained solutions allowing the calculation of the weight loss during pyrolysis of repetitive polymers.

Zip length $1/\gamma$ vs. x^0	Initiation	Termination	MW distribution	Weight loss rate* ($M1 = W/M$)	DP variation in time $x = DP = M1/Mo$
$1/\gamma < x^0$ short	random	first order	any	$\frac{dM1}{dt} = -2ks(1/\gamma) M1$	$\frac{1}{x} - \frac{1}{x^0} = ks t$
$1/\gamma < x^0$ short	random	disprop.	any	$\frac{dM1}{dt} = -2ks(1/\gamma) M1$	$\frac{1}{x} - \frac{1}{x^0} = ks t$
$1/\gamma < x^0$ short	random	recombin.	most probable	$\frac{dM1}{dt} = -4ks(1/\gamma) M1$	$\ln\left(\frac{x}{x^0}\right) = -2ks(1/\gamma) t$
$1/\gamma > x^0$ long	random	any	monodisperse	$\frac{dM1}{dt} = -ks x^0 M1$	$x = x^0$
$1/\gamma > x^0$ long	random	any	most probable	$\frac{dM1}{dt} = -2 ks x M1$	$\frac{1}{x} - \frac{1}{x^0} = ks t$
$1/\gamma < x^0$ short	end scission	first order	monodisperse	$\frac{dM1}{dt} = \frac{-ke}{x \gamma} M1$	$x - x^0 = -2ke(1/\gamma) t$
$1/\gamma < x^0$ short	end scission	first order	most probable	$\frac{dM1}{dt} = \frac{-ke}{x^0 \gamma} M1$	$x = x^0$
$1/\gamma < x^0$ short	end scission	disprop.	monodisperse	$\frac{dM1}{dt} = \frac{-ke}{x \gamma} M1$	$x^0 - \sqrt{x x^0} = 1/2 ke(1/\gamma) t$
$1/\gamma < x^0$ short	end scission	disprop.	most probable	$\frac{dM1}{dt} = \frac{-ke}{x^0 \gamma} M1$	$x = x^0$
$1/\gamma < x^0$ short	end scission	recombin.	most probable	$\frac{dM1}{dt} = -(ke/2) M1$	$\ln\left(\frac{x}{x^0}\right) = -1/4 ke t$
$1/\gamma > x^0$ long	end scission	any	any	$\frac{dM1}{dt} = -ke M1$	$x = x^0$

* ke is the rate constant for the end scission initiation reaction, ks is the rate constant for the random scission initiation reaction, and M the molecular mass of the monomer.

As seen in Table 2.3.2, a plot of $1/DP$ against time will be almost linear, assuming a small zip length and a random initiation reaction. When the initiation reaction is an end scission, or when the termination is a recombination reaction, other dependencies must be applied.

Continuous effort has been put in the understanding and modeling of the pyrolysis of polymers. Since the process is chemically complex and may involve reactions in solid phase, the problem is still a challenge. Modeling of the pyrolysis process for a single class of compounds with low MW has been proven more successful. A computer aided design describing pyrolysis at low temperature (below 400 °C) for alkanes led to a good agreement between the experimental and simulated values both for reactants and products formed. In this program, the pyrolysis mechanism is generated by writing systematically all the generic reactions, including initiations, isomerizations, decompositions by β -scission, metatheses, additions and terminations. To this, secondary mechanisms coupled with the relevant thermochemical and kinetic data are added. Specific heats, standard enthalpies of formation and entropies of molecules, and radicals and kinetics data for each reaction are calculated automatically using

various software or correlations. This system has been tested by modeling the pyrolysis of hexane and tetradecane at low temperature, around 400 °C [26].

- Pyrolysis kinetics for uniform repetitive polymers generating volatile monomer and volatile oligomers

The case of pyrolysis kinetics for a polymer that generates besides the monomer other volatile molecules will be discussed only for a monodisperse linear polymer that has initially P_N molecules, each molecule containing N monomer units. During pyrolysis, the bonds that are cleaved in the polymer at any time can be characterized by the probability of an initial bond to be cleaved, which is given by the fraction:

$$\alpha = \frac{N - n}{N - 1} \quad (2.3.80)$$

where n is the number of monomer units in a polymeric fragment. The probability of a bond to be uncut will be given by $(1 - \alpha)$. Considering the overall rate of cleavage of the first order, the reaction rate can be expressed by the relation:

$$\frac{d\alpha}{dt} = k(1 - \alpha) \quad (2.3.81)$$

or in the integral form:

$$(1 - \alpha) = \exp(-k t) \quad (2.3.82)$$

The formation of molecular fragments P_n ($n < N$) takes place in two different ways. One possibility is the formation of the fragment from one cut at the end of the polymeric chain (somewhat equivalent to an end scission). The other possibility is the formation of the fragment from two cuts within the chain limits. The probability of forming a fragment molecule of n units by the one cut at the "end procedure" is given by the probability of one cut, multiplied by the probability that $n - 1$ bonds remain uncut, multiplied by 2 since there are two polymer ends. This gives for the number of molecules of length n existent in the system at a given moment t the following expression:

$$P'_n = P_N 2 \alpha (1 - \alpha)^{n-1} \quad (2.3.83a)$$

The probability of forming molecules of length n by the second procedure will be given by the multiplying of the probability of one cut with the probability of $(n-1)$ uncut bonds, and with the probability of another cut, which will give $\alpha^2 (1 - \alpha)^{n-1}$. However, a cleavage too close to the polymer end is not acceptable if cannot generate a fragment n monomer units long. The number of good starting points is $(N - n) - 1$. Therefore the number of fragment molecules generated by the second procedure (at the moment t) is given by the formula:

$$P''_n = P_N (N - n - 1) \alpha^2 (1 - \alpha)^{n-1} \quad (2.3.83b)$$

The total number of fragments of n units P_n is given by the sum of rel. (2.3.83a) and (2.3.83b), which gives:

$$P_n = P_N \alpha (1 - \alpha)^{n-1} [2 + (N - n - 1) \alpha] \quad (2.3.83c)$$

The number of remaining molecules of length N at moment t of the pyrolysis process will be given by:

$$P(n=N) = P_N (1 - \alpha)^{N-1} \quad (2.3.84)$$

Assuming that among the fragment molecules all molecules of length L and smaller are volatile, while the other, which are longer than L , are not volatile, the number of monomer units remaining in the polymer sample is, in this case,

$$M_1 = \sum_{n=L+1}^N n P_n \quad (2.3.85)$$

The summation in rel. (2.3.85) leads finally to the expression:

$$M_1 = NP_N \frac{(1 - \alpha)^{L-1}}{L} [N + \alpha(N - L)(L - 1)] \quad (2.3.86)$$

Assuming first order scission and using rel. (2.3.82) for $(1 - \alpha)$, rel. (2.3.86) can be differentiated as a function of t . It is possible in this way to further obtain the variation in weight of the sample based on rel. (2.3.73). It can be shown that the following expression can be obtained:

$$\frac{dM_1}{dt} = -k[(L - 1)M_1 - \frac{(1 - \alpha)^L (N - L)(L - 1)}{N}] \quad (2.3.87)$$

The maximum (absolute) value of the decomposition rate can be obtained in respect to α for rel. (2.3.87) (by making the derivative to α equal to 0). The resulting value is given by the expression:

$$\alpha_{\max} = \frac{N - 2L + 1}{L(N - L)} \quad (2.3.88)$$

and $\alpha_{\max} \approx 1/L$ for $N \gg L$. These values can be introduced in rel. (2.3.86) or (2.3.87) for the estimation of maximum rate of weight loss. The weight loss rate goes first to a maximum given by rel. (2.3.88) and then decreases. This is easily explained by the fact that initially most fragments are too big to evaporate. Then, many molecules with lower mass are generated and they start evaporating. The decreasing number of polymeric molecules makes the rate slow down further on in the process [23].

References 2.3

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2.4 PREDICTION OF PYROLYSIS OUTCOME FROM THERMOCHEMICAL KINETIC CONSIDERATIONS

- General aspects

Pyrolysis is a complex process, and its outcome can be evaluated based on the values of the kinetic parameters controlling the concurring chemical reactions. On the other hand, the kinetic parameters depend on thermodynamic stability of different participating molecules in the thermal degradation. This explains the necessity to use "thermochemical kinetics" concepts [1] for the study of pyrolytic processes. Considering for example a simple reaction of the form:



with the forward rate constant k_1 and the reverse rate constant k_{-1} based on the law of chemical equilibrium (Guldberg and Waage), these rate constants are related to the equilibrium constant K_c by the expression:

$$K_c = \frac{[C][D]}{[A][B]} = \frac{k_1}{k_{-1}} \quad (2.4.2)$$

From rel. (2.2.23) for the expression of equilibrium constant, and from Arrhenius equation given by rel. (2.3.5) for the two kinetic constants, the following relations between the kinetic and thermodynamic parameters can be obtained based on rel. (2.4.2):

$$\Delta H^0 = E_{\text{forward}}^{\#} - E_{\text{reverse}}^{\#} + (\Delta n) RT \quad (2.4.3a)$$

$$\Delta S^0 = R \ln(A_{\text{forward}}/A_{\text{reverse}}) + (\Delta n) R [1 + \ln(R^*T)] \quad (2.4.4a)$$

Rel. (2.4.3a) and (2.4.4a) can be written such that to separate the variables necessary in the calculation of kinetic constants. This will lead to:

$$E_{\text{forward}}^{\#} - E_{\text{reverse}}^{\#} = \Delta H^0 - (\Delta n) RT \quad (2.4.3b)$$

$$\ln(A_{\text{forward}}/A_{\text{reverse}}) = \Delta S^0 / R - (\Delta n) [1 + \ln(R^*T)] \quad (2.4.4b)$$

The Δn correction term to account for the change in the number of moles in the stoichiometric equation for the reaction is necessary because the thermochemical quantities are tabulated for a standard state at 1 atm., while the rate constants are expressed in concentration units (see also rel. 2.2.24). Because of this convention two constants are necessary, $R = 1.987 \text{ kcal mol}^{-1}$, and $R^* = 0.082 \text{ L mol}^{-1} \text{ deg}^{-1}$.

Rel. (2.4.3b) and (2.4.4b) do not provide independent values for the activation energy $E^{\#}$ and for the frequency factor A in Arrhenius equation, which can be written in the form:

$$\log(k) = \log A - E^{\#}/(2.303 RT) \quad (2.4.5)$$

(where the notation \log is used for \log_{10} while \ln has been used for \log_e). However, the values of two unknowns in each of the equations (2.4.3b) and (2.4.4b) allow the calculation of the third one. Since ΔH^0 and ΔS^0 are frequently available in literature, and some direct results can be obtained for either the forward reaction or for the reverse reaction, the calculation of the third parameter is possible in many cases. This procedure is discussed further for different types of reactions involved in a pyrolysis process.

- β -Eliminations not involving a free-radical mechanism

Some reactions taking place during pyrolysis occur through an E_i mechanism (see Section 2.1). These reactions are not slowed down by free radical inhibitors, and therefore they do not involve free radicals. Typical reactions of this type are eliminations of small molecules such as HX ($X = F, Cl, Br$), water, methanol, ammonia, CO , CO_2 , etc. from the polymer side groups. A typical example of elimination reaction can be represented schematically by the equation:



If a free radical mechanism is not involved in the reaction, and it takes place by an E_i mechanism, it is a one-step reaction, with the energy profile along the reaction coordinate illustrated in Figure 2.4.1. The energy of activation $\Delta E^{\#}$ is the result of

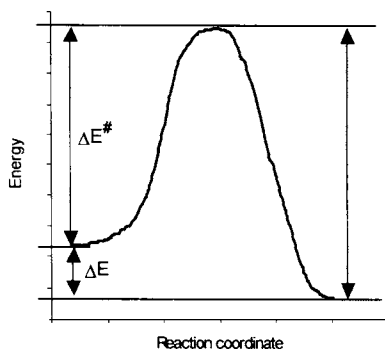
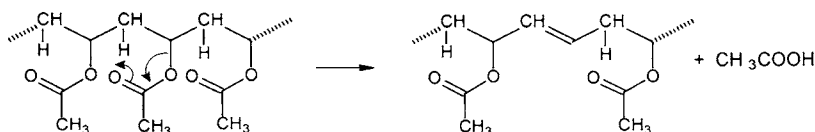


FIGURE 2.4.1. Energy profile for a reaction without an intermediate state.

differences in the bond energies, bond strain, resonances, between the starting compound and the transition state, etc. The entropy of activation is not significantly modified by a modification in the number of components since the transition state implies one single compound. However, ring closures and the constraint of assuming a specific arrangement in space that leads to the reaction may be prohibitive for some reactions. In other cases, the transition state may have more disorder than the starting compound and the entropic factor is favorable. The total reaction enthalpy is not compensated by the formation of a C=C double bond since the reaction occurs with the cleavage of a C—C bond that has more energy

than the second connection in a double bond. Only the high stability of the small molecule formed (HCl, H₂O, CO₂, etc.) ensures that the reaction is possible thermodynamically. Since the overall reaction leads to the formation of two molecules from one, the overall entropy is favorable and an increase in temperature enhances the role of the entropic factor. This explains why these types of reactions are favored by the temperature increase and occur in pyrolytic processes. However, if neither forward values nor reverse values for E^\ddagger and A are known, it is not possible to estimate the value for k .

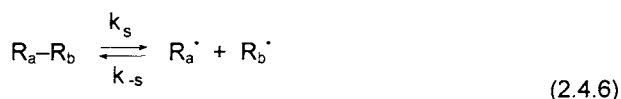
An possible example of a reaction that occurs as a β -elimination is the formation of acetic acid from poly(vinyl acetate) (see Section 6.5). The reaction is shown below:



The thermodynamic parameters for a model reaction of elimination of one molecule of acetic acid from a trimer of vinyl acetate are the following: ΔH_f° (trimer) = -259.7 kcal mol⁻¹, ΔS_f° (trimer) = 156.7 cal T⁻¹ mol⁻¹, ΔH_f° (5-acetyloxyhex-3-enyl acetate) = -166.0 kcal mol⁻¹, ΔS_f° (5-acetyloxyhex-3-enyl acetate) = 135.7 cal T⁻¹ mol⁻¹, ΔH_f° (acetic acid) = -97.1 kcal mol⁻¹, ΔS_f° (acetic acid) = 67.5 cal T⁻¹ mol⁻¹. This leads to the following values for the reaction: $\Delta H^\circ = -3.4$ kcal mol⁻¹ and $\Delta S^\circ = 46.5$ cal T⁻¹ mol⁻¹. The reaction of elimination of acetic acid is only slightly exothermic, indicating that $E_{\text{forward}}^\ddagger \approx E_{\text{reverse}}^\ddagger$. However, ΔS° is considerably high. The value $\Delta n = 1$ shows that the A value slightly decreases with the increase in temperature. However, $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$ increases as T increases and the equilibrium is displaced toward the elimination of acetic acid.

- Initiation reactions in free radical formation during pyrolysis

Many pyrolysis reactions take place with a free radical mechanism. Initiation reaction with the formation of free radicals is therefore an important component in the pyrolysis process. Typically the initiation occurs with the formation of free radicals by a scission reaction (homolysis) of the type:



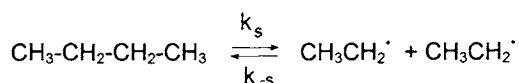
The thermochemistry of this reaction, which consists of the scission of a chemical bond under the influence of heat, has been discussed in Section 2.2. The kinetics of the reaction is sensitive to the stability of the radicals involved in the process. The reverse reaction (k_{-s}) is highly exothermic, and radical-radical combination is not kinetically controlled. For this reason, $E_{\text{reverse}}^\# \approx 0$, and

$$E^\# = E_{\text{forward}}^\# = \Delta H^0 - RT \quad (2.4.7)$$

From rel. (2.4.6) it results that ΔH^0 for the reaction indicated by rel. (2.4.6) gives a reasonable approximation for the formation of the radicals necessary for the initiation process. In other words, rel. (2.2.29) provides one of the necessary parameters in Arrhenius equation for quantitative information on k_s .

Also, ΔS^0 for the scission reaction is positive since one molecule generates two (radical) molecules and $\Delta n = 1$. The value for A_{reverse} can be estimated as equal to the value of A for the radical combination reaction, which occurs for every radical-radical encounter (in singlet state). This leads to $A_{\text{reverse}} \approx 10^{10} \text{ s}^{-1}$ and, using rel. 2.4.4b), to values $A_{\text{forward}} \approx 10^{16} - 10^{17} \text{ s}^{-1}$ [1].

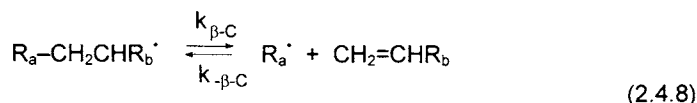
Using the example of n-butane [1], the following reaction can take place under the influence of heat:



From Table 2.2.3, ΔH^0 (C-C) for n-butane is $81.6 \text{ kcal mol}^{-1}$. For a temperature of 800°K , rel. (2.4.7) leads to $E^\# = 81.6 - 1.6 = 80.0 \text{ kcal mol}^{-1}$. For the combination of ethyl radicals $A_{\text{combination}} = A_{\text{reverse}} = 1.12 \cdot 10^{10}$ and ΔS^0 (C-C) $43.9 \text{ cal mol}^{-1} \text{ deg}^{-1}$ [1]. This will lead, based on rel. (2.4.4b), to $A_{\text{forward}} = 10^{17.4} \text{ s}^{-1}$. These estimations generate the following expression for the rate constant k_s for the formation of ethyl radical from butane: $\log(k_s) = 17.4 - 80.0 / (2.303 RT)$. An experimental value for high pressure limit is given by: $\log(k_s) = 16.3 - 81.3 / (2.303 RT)$ [1].

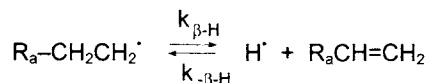
- Propagation reactions in free radical reactions during pyrolysis

There are several ways in which the propagation reaction can take place in pyrolysis. One common propagation reaction is β -scission. An example of β -scission can be written schematically as follows:



The reverse reaction rate constant $k_{-\beta\text{-C}}$ in the equilibrium given by rel. (2.4.8) should be large. The radical addition to an atom involved in a double bond is a strongly exothermic process because of the formation of a C–C bond, which well compensates the opening of a C=C double bond. However, the reverse reaction has an unfavorable entropy loss, because $\Delta n = -1$. As temperature will increase, the $T \Delta S^\circ$ value will become larger than ΔH° leading to a negative ΔG° . This justifies the occurrence of this reaction in many pyrolytic processes. For the example of n-butane, the reaction $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\cdot \rightleftharpoons \text{CH}_3\text{CH}_2\cdot + \text{CH}_2\text{=CH}_2$ has $\Delta H^\circ = 22.7 \text{ kcal mol}^{-1}$ and $\Delta S^\circ = 31.4 \text{ cal mol}^{-1} \text{ deg}^{-1}$. For a temperature of 298° K , this leads to $\Delta G^\circ = 13.3 \text{ kcal mol}^{-1}$, indicating that practically the reaction does not take place. However, for 800° K the value becomes $\Delta G^\circ = -2.4 \text{ kcal mol}^{-1}$, which shows that when the temperature is high enough, the reaction takes place. The thermochemical balance based on rel. (2.4.3b) and (2.4.4b) predicts $\log(k_{\beta\text{-C}}) = 8.95 - 7.6/(2.303 RT)$, which is close to reported experimental values of $\log(k_{\beta\text{-C}}) = 8.5 - 7.7/(2.303 RT)$ [2]. Information on the enthalpy of reaction for various olefins with small radicals (reverse β -scission) is available in literature [3].

The radical expelled by β -scission can be H following a reaction of the following type:



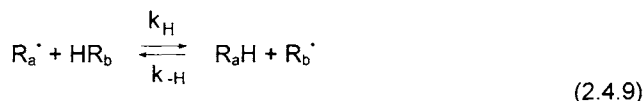
This type of reaction is slower than the loss of an alkyl radical, and $k_{\beta\text{-H}} < k_{\beta\text{-C}}$, since C–H bonds are stronger than C–C bonds. For hydrogen radical elimination it has been estimated a rate constant given by the expression $\log(k_{\beta\text{-H}}) = 14.0 - 38.3/(2.303 RT)$. Also, it was estimated that $k_{\beta\text{-H}} / k_{\beta\text{-C}} \approx 2.82 \exp(-9600/RT)$ [1].

For the case where a heteroatom such as oxygen is in a γ -position to the atom bearing the radical, a heteroatom bearing the radical can be expelled. The rate constant is between 1/2 and 1/10 of those for an alkyl radical. Also, if an oxygen is in a β -position to the atom bearing the radical, a carbonyl compound is typically formed and not an olefin. This reaction is typically influenced by the thermodynamic stability of the compounds, and a larger difference between the C–O and C=O bond compared to the difference between C–C and C=C bond favors the formation of the carbonyl compound. The rate of reactions that are more favored thermodynamically seems to be higher than that for thermodynamically unfavorable reactions. Two variants of scission for oxygen-containing radicals are particularly rapid at elevated temperatures. These are decarboxylation and decarbonylation. The reactions are shown below:



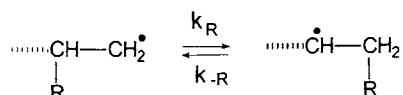
Decarboxylation is more rapid than decarbonylation, and more rapid for R = alkyl vs. R = aryl. The rate constant for decarboxylation is estimated for R = methyl to be approximated by $\log(k) = 13.3 - 6.2/(2.303 RT)$, and for R = phenyl is estimated by $\log(k) = 12.6 - 8.6/(2.303 RT)$.

Another important propagation reaction during pyrolysis is *hydrogen abstraction*. This reaction can be written schematically as follows:

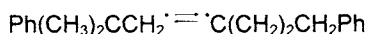


In the hydrogen abstraction, a transition state of the type $\text{R}_a\text{HR}_b^\ddagger \equiv \text{R}_a^{+\delta}\text{HR}_b^{-\delta}$ is present, and the activation energy E_H^\ddagger is only a small fraction of $\Delta H^0(\text{R}_a\text{-H})$, being estimated at less than 12% of the energy necessary for the C-H bond cleavage. Hydrogen abstraction is a bimolecular process requiring the collision of R_a^\bullet and HR_b , and has a negative entropy. For this reason the A factor for the forward reaction is in general low, and typically $A_{\text{forward}} \approx 10^8 - 10^9 \text{ s}^{-1}$. An exception to this situation is the formation of molecular hydrogen by hydrogen abstraction, when $A_{\text{forward}} \approx 10^{10} - 10^{11} \text{ s}^{-1}$.

Rearrangements consisting, for example, of intermolecular 1,2-shifts are also possible for the radicals, as schematically shown below:



However, this reaction is not likely for R = alkyl, because it has a large activation barrier. For R = aryl the reaction is possible, and, for example, the reaction shown below:

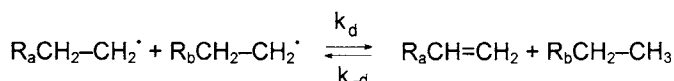


has $\Delta H^0 = -5 \text{ kcal mol}^{-1}$ and $\log(k) = 11.55 - 11.8/(2.303 RT)$.

- Termination reactions in free radical reactions during pyrolysis

Two main types of terminations take place in free radical reactions during pyrolysis, namely combination and disproportionation. The radical-radical combination takes place with almost zero activation energy E^\ddagger . The reaction rate already discussed as the reverse reaction of scission has a typical rate constant $k \approx 10^{9.5} - 10^{10} \text{ s}^{-1}$.

Disproportionation reaction is a bimolecular process that can be expressed by the reaction of the type:



where R_a and R_b can be the same or different. Because the activation energy for the radical combination is usually close to zero ($E_{\text{forward}} \approx 0$), and $\Delta n = 0$, the result indicates $E_{\text{reverse}} \approx -\Delta H^0$. Considering the example of disproportionation of two ethyl radicals, $\Delta H^0 = -65.5 \text{ kcal mol}^{-1}$, and $A \approx 10^{9.2} \text{ s}^{-1}$. [1]. The ratio k_d/k_{-d} varies from radical to radical, and values between 0.004 to 3.0 are reported in literature [4].

Thermochemical kinetic considerations for chain scission reactions

Most chemical transformations in a chain scission reaction result from the propagation steps. The initiation steps maintain a low steady state concentration of free radicals, and its rate is compensated by the termination steps. However, as seen in Table 2.3.2, the variation in the weight of sample during pyrolysis is frequently determined by the initiation step (random scission or end scission). The rate constant for the initiation plays a critical role in controlling the overall reaction rate. Nevertheless, the full kinetic process incorporates more than one kinetic constant. Also, the same initial compound may undergo more than one reaction path, various paths being competitive to each other. Changes in pyrolysis conditions, mainly in the pyrolysis temperature, may favor one path or the other, leading to different results in pyrolysis composition.

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CHAPTER 3

*Review of Analytical Pyrolysis Instrumentation***3.1 PARAMETERS CONTROLLING THE ANALYTICAL PYROLYSIS PROCESS****- General aspects**

Analytical pyrolysis requires heating of the sample at a temperature significantly higher than ambient. Commonly selected temperatures are between 500° C and 800° C, but for special purposes this temperature can be higher or lower. The pyrolytic process is done in a pyrolysis unit (pyrolyzer), which has a source of heat. The pyrolyzer is interfaced on-line or off-line with an analytical instrument, which is used for the measurement of the pyrolysis products. Common techniques applied for this purpose are gas chromatography (GC), gas chromatography/mass spectrometry (GC/MS), mass spectrometry (MS), etc. Pyrolysis GC/MS (Py-GC/MS) is probably the most common technique in analytical pyrolysis.

Commonly, analytical pyrolysis is performed as *flash pyrolysis*. This is carried out with a fast rate of temperature increase, of the order of 10,000° C/s, targeting isothermal conditions at a temperature where the sample is completely pyrolyzed. After the final pyrolysis temperature is attained, the temperature is maintained essentially constant (*isothermal pyrolysis*). Special types of analytical pyrolysis also are known. One example is *fractionated pyrolysis*, in which the same sample is pyrolyzed at different temperatures for different times in order to study special fractions of the sample. Another special type is *stepwise pyrolysis*, in which the sample temperature is raised stepwise and the pyrolysis products are analyzed between each step. *Temperature-programmed pyrolysis*, in which the sample is heated at a controlled rate within a temperature range, is another special type. This type of pyrolysis can be used for analytical purposes but is not very common.

There are several construction principles for pyrolyzers, such as with resistively heated filaments, inductively heated, furnace type, and radiatively heated. Detailed descriptions for instrument construction can be found in literature [1] or obtained from instrument manufacturers. The pyrolysis unit usually consists of a controller and the pyrolyzer itself. The controller provides the appropriate energy needed for heating. A simplified scheme of a pyrolyzer based on the design of a flash heated filament system (made by CDS Inc.) is shown in Figure 3.1.1.

The pyrolyzer body (or the housing) consists of a small chamber that is heated in order to avoid condensation of the pyrolysates on the housing walls. The housing temperature is typically not higher than 200–250° C and its walls are not in contact with the sample. Inside the pyrolyzer housing, a probe insert can be introduced or removed. The tip of the probe insert has the heating element and a sample holder. The heating element consists of a coil or a ribbon filament (typically made from platinum) that can reach the desired pyrolysis temperature when electrical current from the controller is passed through it. The sample holder is usually a quartz tube or boat where the small sample is deposited for analysis. A stream of inert gas flows through the housing carrying the pyrolysates to the analytical instrument. The stream of gas inside

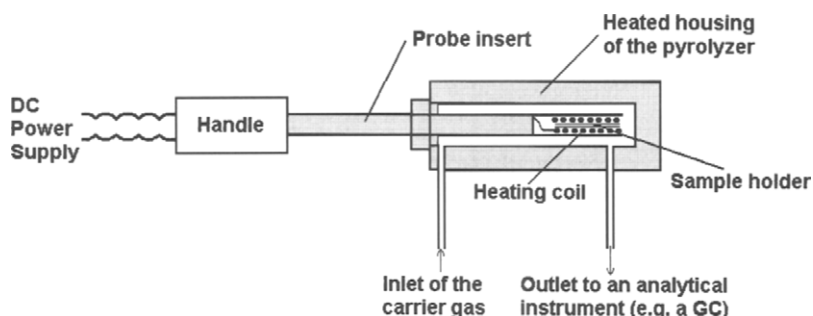


FIGURE 3.1.1. *The simplified scheme of a pyrolyzer (based on the design of a heated filament system made by CDS Inc.).*

the pyrolyzer can be used further as a carrier gas if the pyrolyzer is interfaced with an analytical instrument such as a gas chromatograph.

A primary requirement for the pyrolysis units used for analytical purposes is that of reproducibility [2, 3]. One condition for achieving reproducibility is to use a precisely controlled temperature [4, 5]. The targeted isothermal condition for flash pyrolysis is referred to as *equilibrium temperature* (T_{eq}). The T_{eq} is also named *final pyrolysis temperature* because in practice it is not possible to heat a sample instantly to T_{eq} , although very short times for reaching T_{eq} can be achieved. Because pyrolysis is frequently a complex process, there is no precise rule to indicate which T_{eq} temperature should be chosen for a given sample. This value may depend on the material to be pyrolyzed and on the scope of the analysis. The ceiling temperature $T_c = \Delta H^0 / \Delta S^0$ for the polymer (see rel. (2.2.30)) may be used as a guide for choosing T_{eq} , but T_c was not proven in practice as a very good estimation for this choice. For this reason, in the specialized literature the description of the pyrolysis products of a certain material is almost always associated with the description of experimental conditions for the pyrolysis including the value for T_{eq} . This temperature should be selected at about 100° C higher than the ceiling temperature.

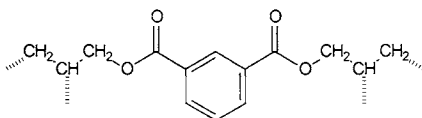
Another parameter selected for analytical pyrolysis experiments is the *temperature rise time* (TRT). This parameter measures the time necessary for the heating element of the pyrolyzer to reach T_{eq} . The goal in flash pyrolysis is to have a very short TRT, such that the decomposition of the sample takes place, virtually, in isothermal conditions. However, this requirement may be difficult to achieve. One more parameter used for the control of the pyrolytic process is the *total pyrolysis time* (or *total heating time* THT), which is the sum of TRT with the time of maintaining the sample at T_{eq} . This parameter should be chosen long enough for the total amount of sample to be pyrolyzed during THT. Because longer THTs than those exactly needed for the pyrolysis of the sample are commonly used, this parameter is not critical as long as the whole sample is pyrolyzed within THT. The value for THT is typically much longer than TRT.

Another important factor in achieving reproducibility in analytical pyrolysis is the pyrolyzer construction. Several pyrolyzer types are commercially available, and also some unique setups were developed and reported. Various types of common pyrolyzers are further discussed in Section 3.2.

- Equilibrium temperature T_{eq}

Depending on the nature of the sample (polymer), pyrolysis parameters influence more or less the result of an analytical pyrolysis experiment. For example, some polymers are particularly resistant to thermal decomposition. These are usually polymers with the backbone containing more than one bond, with large number of aromatic rings in the backbone, or with a tridimensional structure. Among these are compounds such as poly(*p*-phenylene), poly(oxy-1,4-phenylene), poly(thio-1,3-phenylene), as well as several compounds containing heterocycles in the backbone (see Table 14.1.1). For the polymers more resistant to heat, a higher temperature is usually selected as T_{eq} for analytical pyrolysis experiments. A temperature T_{eq} around 850° C is typically sufficiently high to decompose even very stable polymers. However, this temperature may be unnecessarily high for other polymers that decompose easily around 300° C. An excessively high temperature may diminish the chance of detecting some structural characteristics that can be obtained only from the study of the dimers, trimers, tetramers, etc. of the polymer. If only the monomer and small molecules are generated during pyrolysis, information on properties such as stereospecificity or copolymeric structure is lost. For this reason, T_{eq} values around 600° C may be more appropriate for certain studies using analytical pyrolysis.

The variability in analytical pyrolysis results as a function of equilibrium temperature T_{eq} in the pyrolysis of a polymer is further exemplified for poly(diallyl isophthalate), which has the idealized structure shown below:



The polymer has a crosslinked structure, and the curve showing the variation of weight loss % as a function of temperature (thermogravimetric analysis or TGA curve) is given in Figure 3.1.2. The sample was heated in N_2 between 30° C and 830° C at a heating rate of 10° C/min.

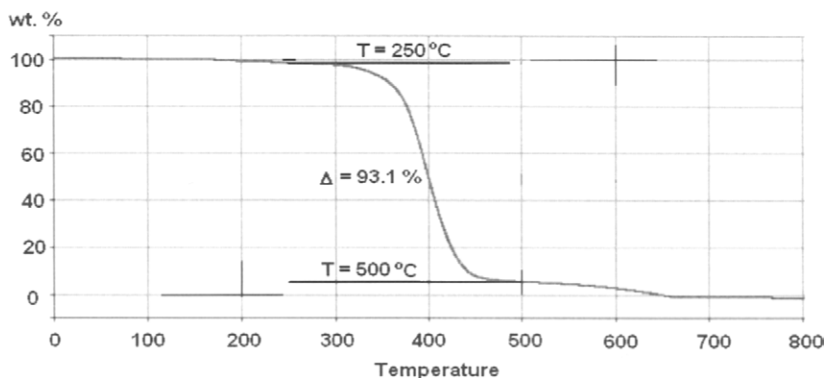


FIGURE 3.1.2. Variation of weight % loss for a poly(diallyl isophthalate) sample in a TGA experiment at a heating rate of 10° C/min.

The thermogram shows that the polymer starts decomposing around 300° C, and, therefore, a choice of $T_{eq} = 600^{\circ}\text{C}$ would be sufficiently high for the complete polymer decomposition. The decrease in weight seen on the TGA curve at temperatures higher than 500° C is probably due to the oxidation of the resulting char in the presence of traces of oxygen in the inert atmosphere of the thermal analysis instrument. Pyrolysis of 0.4 mg poly(diallyl isophthalate) with $M_w = 500,000$ performed at 600° C in He at a heating rate of 20° C/ms with the analysis of the pyrolysate done on-line by GC/MS (see Section 3.2) gives the pyrogram shown in Figure 3.1.3. The separation was done on a Carbowax column (60 m, 0.32 mm i.d., 0.32 μm film thickness) with the GC starting at 40° C with a ramp of 2° C/min. up to 240° C and a final oven time of 20 min. The detection was done using a mass spectrometer (MS) operated in EI+ mode.

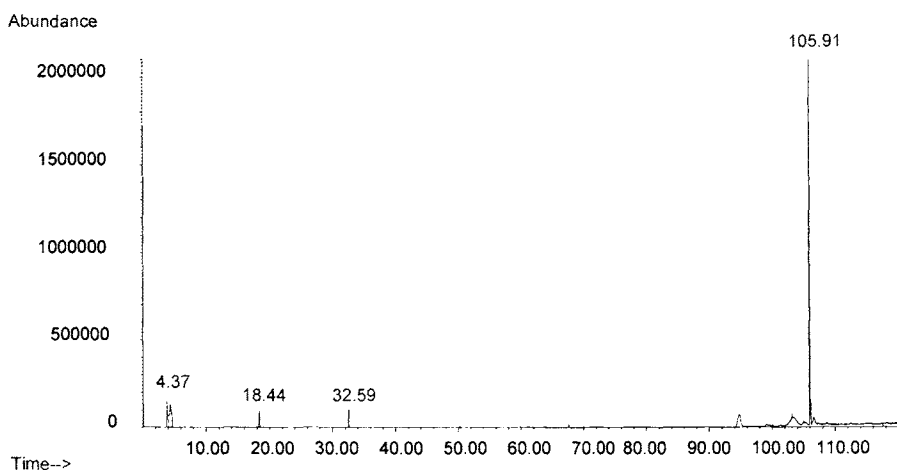


FIGURE 3.1.3. Result for a Py-GC/MS analysis of poly(diallyl isophthalate). Pyrolysis done on 0.4 mg material at 600° C, with the separation on a Carbowax type column.

The peak identification for the chromatogram shown in Figure 3.1.3 was done using MS spectral library searches and is given in Table 3.1.1. The table indicates the compound name for a specific peak, as well as the peak retention time, the molecular weight MW of the compound, and the area % in the chromatogram. The masses of molecules can be calculated using two different conventions. One convention considers the natural isotopic abundance of elements. The other convention considers only the masses of the most abundant isotope, which is useful for MS interpretations. For this latter case, the resulting mass is rounded to the unit [6]. The masses given in the tables showing peaks identifications will use the convention of the most abundant isotope, unless otherwise specified. Also, the notation for the mass used in this book is MW (molecular weight), which should be differentiated from M_w used for weight average molecular mass (see rel. 1.1.3).

TABLE 3.1.1. *Compounds identified in the pyrogram of poly(diallyl isophthalate) shown in Figure 3.1.3 and performed at 600° C.*

Peak	Compound	Ret. time	MW	Area %
1	carbon dioxide	4.37	44	15.58
2	water	18.44	18	3.47
3	styrene	32.59	104	2.58
4	benzoic acid 2-propenyl ester	67.45	162	0.76
5	diethylene glycol dibenzoate	103.05	314	8.56
6	1,4-benzendicarboxylic acid di-2-propenyl ester	105.91	246	69.05

As seen from Figure 3.1.3 and Table 3.1.1, only a few compounds are generated during pyrolysis (the origin of styrene is not clear, and it can be an impurity in the polymer or a different contamination). A considerable proportion of the decomposition products consist of monomer.

When the pyrolysis of the same polymer is performed at 850° C, a different pyrogram is obtained, as shown in Figure 3.1.4. The separation and detection of the pyrolysis constituents was done in similar conditions as for the experiment at 600° C.

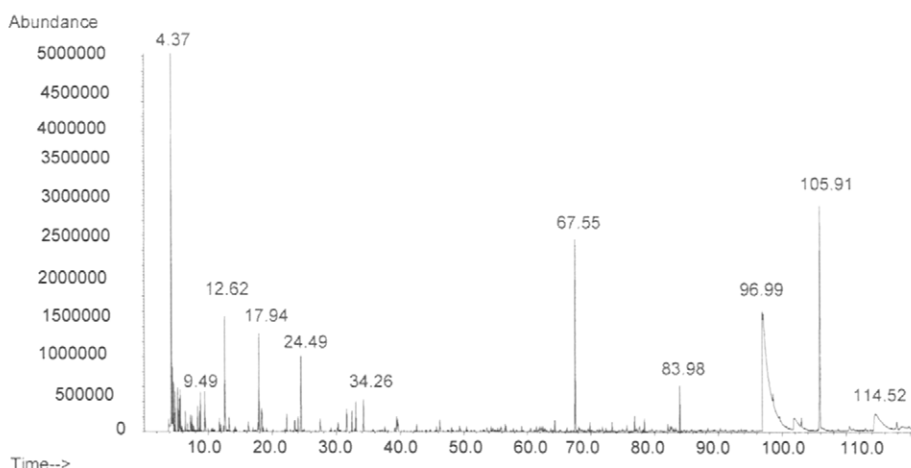


FIGURE 3.1.4. *Result for a Py-GC/MS analysis of poly(diallyl isophthalate). Pyrolysis done on 0.4 mg material at 850° C, with the separation on a Carbowax type column.*

The peak identification for the chromatogram shown in Figure 3.1.4 also was done using MS spectral library searches and is given in Table 3.1.2. The pyrogram at 850° C shows peaks at higher intensity, as can be noticed from the scale of Figures 3.1.3 and 3.1.4 ($2 \cdot 10^6$ and $5 \cdot 10^6$, respectively). Also, a significant number of small molecules and aromatic compounds are present in the pyrolysate at 850° C. Among these are methylpropene, butadiene, benzene, toluene, biphenyl, methylnaphthalene, etc. Some of these compounds are the result of a more thorough cleavage of the polymer molecule, and others, such as methylnaphthalene or biphenyl, are the result of secondary reactions with the formation of more stable molecules at higher temperatures.

TABLE 3.1.2. Compounds identified in the pyrogram of poly(diallyl isophthalate) shown in Figure 3.1.4 and performed at 850° C.

Peak	Compound	Ret. time	MW	Area %
1	carbon dioxide	4.32	44	10.48
2	2-methylpropene	4.49	56	trace
3	1,3-butadiene	4.69	54	0.86
4	1,3-pentadiene	4.93	68	0.47
5	3-methyl-1,4-pentadiene	5.30	82	0.53
6	1,5-hexadiene	5.70	68	1.38
7	1,3-cyclopentadiene	6.47	66	0.35
8	1-methylcyclopentene	6.81	82	0.20
9	2,4-hexadiene	7.27	82	0.48
10	2-methyl-1,3-pentadiene	7.52	82	0.28
11	1,3,5-hexatriene	8.37	80	0.47
12	2-propenal	8.84	56	1.10
13	1,3-cyclohexadiene	9.49	80	1.17
14	3-methyl-1,3,5-hexatriene	11.78	94	0.26
15	benzene	12.62	78	3.20
16	2-methyl-1,3,5-hexatriene	13.29	94	0.43
17	1,3,5-cycloheptatriene	16.32	92	0.32
18	toluene	17.94	92	2.66
19	water	18.36	18	0.81
20	2-propen-1-ol	22.31	58	0.41
21	ethylbenzene	23.53	106	0.34
22	1,2-dimethylbenzene	24.04	106	0.38
23	1,3-dimethylbenzene	24.49	106	1.95
24	1,4-dimethylbenzene	27.51	106	0.43
25	propylbenzene	29.20	120	trace
26	1-ethyl-3-methylbenzene	30.31	120	0.42
27	1,3,5-trimethylbenzene	31.63	120	0.55
28	styrene	32.47	104	0.50
29	2-propenylbenzene	33.06	118	0.84
30	1,2,3-trimethylbenzene	34.26	120	0.88
31	(1-methylethenyl)benzene	37.60	118	trace
32	1-ethenyl-3-methylbenzene	39.46	118	0.94
33	3-butenylbenzene	39.60	132	trace
34	1-propenylbenzene	42.60	118	trace
35	1-ethenyl-3,5-dimethylbenzene	45.54	132	trace
36	2-ethenyl-1,4-dimethylbenzene	46.24	132	0.43
37	1-methyl-2-(2-propenyl)benzene	49.33	132	trace
38	benzaldehyde	50.27	106	0.10
39	propyl benzoate	64.37	164	0.31
40	benzoic acid 2-propenyl ester	67.55	162	5.38
41	1-methylnaphthalene	69.89	142	0.27
42	1,1'-biphenyl	76.90	154	0.41
43	3-methyl-3-buten-1-ol benzoate	78.46	190	0.38
44	3-methyl-1,1'-biphenyl	82.10	168	trace
45	C ₁₃ H ₁₄ O ₂	83.98	202	1.17
46	benzoic acid	96.99	122	36.93
47	dimethylphthalate	98.60	194	3.03
48	diethylphthalate	99.61	222	1.33
49	3-methylbenzoic acid	101.90	136	2.44
50	diethylene glycol dibenzoate	103.02	314	0.66
51	1,4-benzendicarboxylic acid di-2-propenyl ester	105.91	246	8.40
52	3-propen-2-ylbenzoic acid	114.52	162	5.65

Other examples showing the influence of pyrolysis temperature on pyrolysis results are shown later in this book (see e.g. Section 13.4).

The increase in the pyrolysis temperature T_{eq} leads almost invariably to an increase in the pyrolysate amount in Py-GC/MS. This effect may be in some cases only due to a more effective injection of the pyrolysate into the GC system. For many polymers pyrolysis around 600–650° C leads to a complete decomposition, and the nature of the pyrolysate is not significantly influenced by increasing the temperature, for example, with 100° C. For the polymers that are very resistant to heating, a higher temperature is necessary for breaking the macromolecule. An excessively increased temperature, for example around 1000° C is not necessarily recommended since new compounds (e.g. aromatic hydrocarbons) are formed at these temperatures, and in some instances valuable information related to the polymer structure is lost. For certain polymers, larger fragments, if possible to be identified, give a better understanding of the polymer structure.

- Temperature rise time TRT and total heating time THT

The importance of selecting a specific TRT value for an analytical pyrolysis experiment is determined by the fact that during the TRT the decomposition kinetics of the sample is changing. Typically during the temperature rise time (TRT), the kinetic constant k of the reaction will increase. Assuming a linear temperature increase with the rate q and starting at T_0 , the temperature is given at a certain moment t during TRT by the formula:

$$T = T_0 + q t \quad (3.1.1)$$

Based on rel. (3.1.1), assuming a first order reaction where the variation of the sample weight during pyrolysis is given by rel. (2.3.35a), and using rel. (2.3.38) for the differential expression for the weight, the variation in weight can be written in this case as follows:

$$\frac{dW}{dt} = A \exp \left[\frac{-E^\#}{R (T_0 + q t)} \right] W \quad (3.1.2)$$

or separating the variables, rel. (3.1.2) becomes:

$$\frac{dW}{W} = A \exp \left[\frac{-E^\#}{R (T_0 + q t)} \right] dt \quad (3.1.3)$$

Rel. (3.1.3) can be, in principle, integrated for the two intervals of time between $t = 0$ and $t = \text{TRT}$ when the temperature is increased and between $t = \text{TRT}$ and $t = \text{THT}$ when the temperature is kept constant at T_{eq} . A numerical integration can show the variation of W/W_0 for specific values of A , $E^\#$, T_0 , q , TRT, and THT. The values for A and $E^\#$ depend on the compound to be pyrolyzed, while T_0 , q , TRT, and THT are chosen values for each experiment. Figure 3.1.5 shows the variation of W/W_0 for three ideal compounds having the same frequency factor $A = 10^6 \text{ sec}^{-1}$ and different activation energies $E^\#$ (100 kJ/mol, 80 kJ/mol, and 60 kJ/mol). In these examples, $T_0 = 200^\circ \text{C}$, $q = 10^\circ \text{C/ms}$, TRT = 40 ms, and THT = 500 ms.

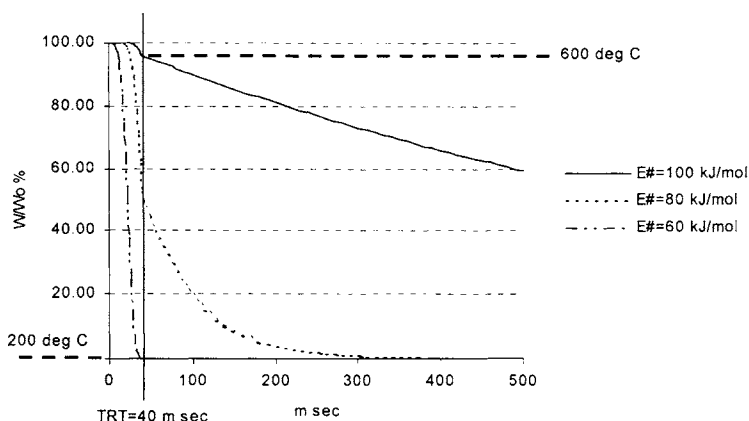


FIGURE 3.1.5. Variation of W/W_o with time for several $E^\#$ values in a hypothetical reaction. Temp. ramp 10°C/msec , starting temp. $T_o = 200^\circ \text{C}$, TRT 40 msec, THT 500 msec.

For some materials, pyrolysis may be effectively complete before equilibrium temperature is attained [7]. This is determined by the nature of each compound reflected in the values of the frequency factor A and activation energy $E^\#$ and is exemplified in Figure 3.1.5 by the curve corresponding to $E^\# = 60 \text{ kJ/mol}$. For a THT = 500 msec, the compounds with $E^\# = 60 \text{ kJ/mol}$ and $E^\# = 80 \text{ kJ/mol}$ are completely decomposed, while the compound with $E^\# = 100 \text{ kJ/mol}$ loses only about 40% of its weight. For a pyrolysis reaction generating only gaseous compounds, this indicates that this THT is too short.

Mainly for samples that decompose rapidly, the heating rate needs to be reproducible, but the related problems for flash pyrolysis are less critical than when using the gradient control. The control of sample temperature in slowly varying non-isothermal conditions is not necessarily harder to achieve than that in isothermal conditions. However, it has been shown [8] that the heating rate during thermal decomposition is a sensitive parameter for reproducibility. Secondary reactions are much more likely to occur in slow gradient pyrolysis. Also, when pyrolytic reactions with different kinetics can occur, a slow heating rate will favor reactions with lower activation energy, while higher temperatures may favor reactions with a higher activation energy and frequency factor (see rel. (2.3.5)) [1]. When the pyrolysis unit is interfaced with an analytical instrument such as a gas chromatograph (GC), pyrolysis in a short time interval is preferred because this will allow the chromatographic separation of the pyrolysate without the supplementary need of a focusing step. When the pyrolysate is generated in a relatively long period of time, a cryofocusing step is commonly used before the chromatographic separation starts. A narrow interval of time in which the sample is introduced into the GC is necessary for maintaining good chromatographic resolution. Long time deliveries of the sample to the GC are avoided in the pyrolyzers designed to provide a well-controlled constant temperature in a very short TRT (flash pyrolysis).

The pyrolyzer construction is important for ensuring a specific rate of reaching the T_{eq} temperature. The pyrolyzer construction may determine the way in which heat is transferred to the sample. The transfer process can be understood by evaluating the heat transfer mechanisms, which are conduction, convection, and radiation. The heat

transfer rate q in J/s = W (watts) by unidirectional conduction for a small element of a material having the area A and thickness dx is given by Fourier's law:

$$q = -k A \frac{dT}{dx} \quad (3.1.4)$$

where k is a conductivity constant expressed in J/(s cm K°) and dT is the infinitesimal temperature difference between the two faces of the material (the minus sign indicates the decrease of the temperature of the heat source). The differential form of rel. (3.1.4) can be integrated for different body shapes (slab, cylinder, hollow cylinder, etc.). In all cases the heat flow depends linearly on the temperature difference across the material.

Convection will be responsible for a heat transfer between a surface and a fluid. The rate of heat transfer will be given in this case by the formula:

$$q = h A \Delta T \quad (3.1.5)$$

where h is the convective (film) heat transfer coefficient expressed in J/(s cm² K°), A is the area of the surface, and ΔT is the temperature difference between the surface and the main body of the fluid. Heat transfer through convection takes more complicated expressions when phase changes (e.g. boiling) occur on the surface.

The heat transfer through radiation between two surfaces at temperatures T_1 and respectively T_2 , both of area A , is given by the formula:

$$q = A \varepsilon \sigma (T_1^4 - T_2^4) \quad (3.1.6)$$

where ε is the emissivity of the two surfaces ($\varepsilon = 1$ for a black body), and where σ is the Stefan-Boltzmann constant $\sigma = 5.67 \cdot 10^{-12}$ J/[s cm² (K°)⁴].

Several aspects of sample heating can be rationalized using the above formulas. For example, rel. (3.1.4) to (3.1.6) indicate that the heat transfer is dependent on the area A through which the heat flows. For conduction, A is the contact area between the sample and the heat source. Therefore, a good contact is useful for this type of heating. When the sample vaporizes, this contact can be easily diminished. The sample conductivity also will play an important role in this type of heating. Heating through convection depends on fluid flow on the hot surface, and this may be low for many solid materials. Heating through radiation is very dependent on temperature (fourth power), but it is not the main heat transfer mechanism at lower temperatures.

- Other parameters affecting analytical pyrolysis

The value of T_{eq} and the conditions of attaining T_{eq} temperature by the sample are not controlled solely by the heat source of the pyrolyzer but also by the sample properties and the pyrolyzer construction [9, 10]. This is caused by the variations in the process of heat transfer to the sample from the heat source. For example, sample characteristics such as the mass m and the specific heat c will influence the increase of the sample temperature by the formula $\Delta T = Q/(m c)$. In addition, phase changes and exothermic and endothermic chemical reactions in the sample may play an important role in temperature rise. To diminish the variations determined by these processes, a very

small sample size is recommended. A study done on the temperature variation of a filament pyrolyzer [11] showed a decrease of the nominal temperature of the filament for the first part of the THT when the sample load increased. This effect was due to heat absorption by the sample. One way to produce a rapid heat transfer to the sample is to diminish the sample size [1, 12]. This implies that the amount of heat required by the sample to reach a certain temperature is small and that the heat can be transferred rapidly. Typical sample sizes in analytical pyrolysis vary from a few μg to a few mg. Assuming a perfect contact between the sample and the heating element of the pyrolyzer, calculations were done to find the transmission of heat into the sample as a function of time and sample layer thickness [13]. For this purpose, it was considered that the heat transfer to the sample takes place only by conductivity, is unidirectional, and follows the simple equation:

$$a \frac{d^2 T}{dx^2} = \frac{dT}{dt} \quad (3.1.7)$$

In rel. (3.1.7) "a" is the thermal diffusivity of the material to be pyrolyzed. The solution of equation 3.1.7 is shown in Figure 3.1.6 for $a = 2 \cdot 10^{-7} \text{ m}^2 / \text{s}$, initial temperature $T_0 = 20^\circ \text{C}$, heating rate $q = 5000^\circ \text{C} / \text{s}$ and $\text{TRT} = 0.1 \text{ s}$, and for three layer thicknesses l of 0.1 mm, 0.25 mm and 0.5 mm.

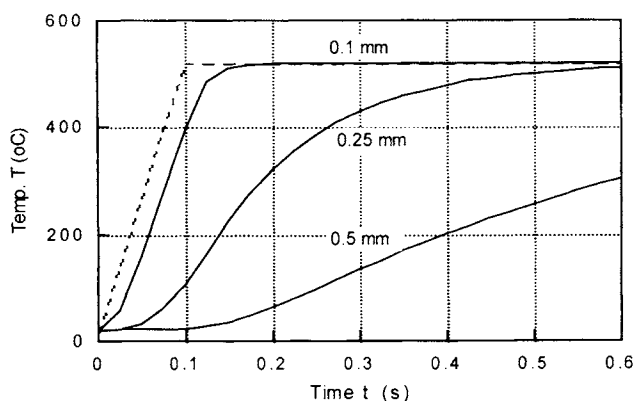


FIGURE 3.1.6. The variation of $T(x, t)^\circ \text{C}$ at $x = 0$ as a function of sample layer thickness, for three layer thicknesses l of 0.1 mm, 0.25 mm, and 0.5 mm. The dotted line shows the temperature of the heating element.

It can be seen from Figure 3.1.6 that considering only the thermal conductivity, the sample temperature increases very slowly compared to that of the heating element (dotted line in Figure 3.1.6) when the sample thickness is not extremely small. Fortunately, other types of heat transfer take place simultaneously to conductivity, and part of this effect is diminished. However, to avoid a temperature gradient in the sample bulk, the sample should cover the heating surface in a thin and uniform film.

The effect of sample size on the pyrolysate composition can be exemplified for the pyrolysis of a poly(vinyl ethyl ether) sample. The polymer has the formula

$[-CH_2CH(OC_2H_5)-]_n$ and CAS# 25104-37-4. The pyrogram shown in Figure 3.1.7 was obtained from 0.4 mg sample at 600° C in He at a heating rate of 20° C/ms with 10 s. THT. The separation was done on a Carbowax column. The peak identification for the pyrogram was done using MS spectral library searches and is given in Table 3.1.3.

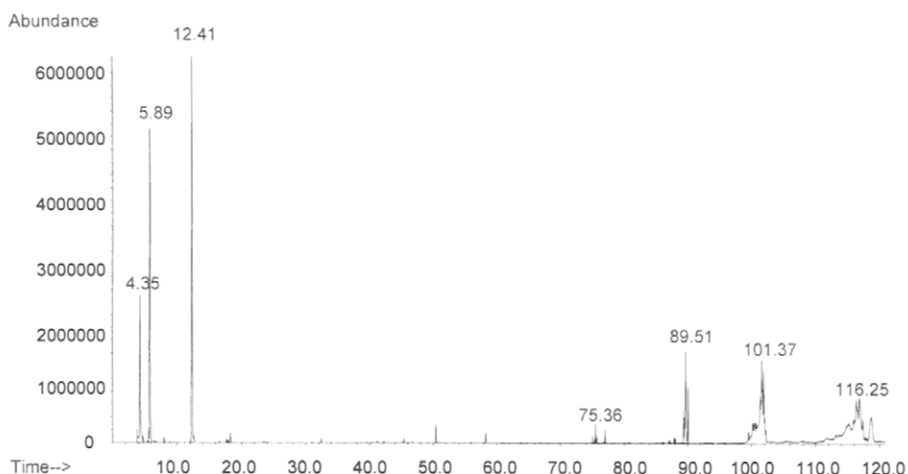


FIGURE 3.1.7. Result for a Py-GC/MS analysis of poly(vinyl ethyl ether) $M_w = 3,800$. Pyrolysis done on 0.4 mg material at 600° C, with the separation on a Carbowax type column.

TABLE 3.1.3. Compounds identified in the pyrogram of poly(vinyl ethyl ether) as shown in Figure 3.1.7.

Peak	Compound	Ret. time	MW	Area %
1	ethane	4.35	30	17.19
2	acetaldehyde	5.89	44	32.05
3	acetone	8.06	58	1.13
4	2-ethoxypentene	9.51	116	0.57
5	ethanol	12.41	45	37.53
6	benzene	12.65	78	trace
7	toluene	17.95	92	trace
8	water	18.34	18	1.00
9	styrene	32.49	104	0.58
10	acetic acid	45.42	60	0.99
11	benzaldehyde	50.44	106	1.57
12	acetophenone	58.30	120	0.81
13	4,6,8,10-tetraethoxydecan-2-one	75.10	332	1.20
14	4,6,8,10-tetraethoxydecan-2-one diastereoisomer	75.59	332	2.59
15	4,6,8,10-tetraethoxydecan-2-one diastereoisomer	75.76	332	1.42
16	phenol	77.06	94	1.37

The increase in the sample size from 0.4 mg to 0.8 mg has a significant effect in the case of this polymer pyrogram (even if this is not the case for every polymer or other instrumental settings). The pyrogram of a 0.8 mg sample of poly(vinyl ethyl ether) is shown in Figure 3.1.8. The identification of the peaks in the pyrogram was done using mass spectral library searches and is given in Table 3.1.4.

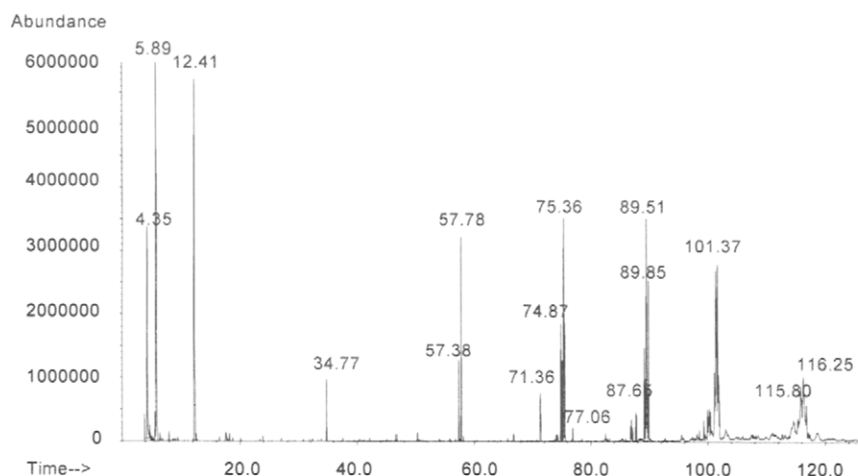


FIGURE 3.1.8. Result for a Py-GC/MS analysis of poly(vinyl ethyl ether) $M_w = 3,800$. Pyrolysis done on 0.8 mg material at 600°C , with the separation on a Carbowax type column.

TABLE 3.1.4. Compounds identified in the pyrogram of poly(vinyl ethyl ether) as shown in Figure 3.1.8.

Peak	Compound	Ret. time	MW	Area %
1	ethane	4.35	30	6.80
2	1,3-butadiene + 1-pentene	4.76	54 and 70	0.45
3	ethoxyethene (monomer)	5.65	72	0.88
4	acetaldehyde	5.89	44	11.99
5	1-heptene	6.43	98	0.00
6	acetone	8.06	58	0.32
7	2-ethoxypentene	9.51	116	0.31
8	ethanol	12.41	46	11.57
9	benzene	12.65	78	0.00
10	toluene	17.95	92	0.00
11	water	18.34	18	0.00
12	1-methoxy-2-propanone ?	27.23	88	0.26
13	styrene	32.49	104	0.00
14	1,3,5-triethoxypentane	34.77	204	1.59
15	1-tridecene	37.52	182	0.00
16	acetic acid	45.42	60	0.00
17	benzaldehyde	50.44	106	0.00
18	4,6,8-triethoxyoctan-2-one	57.38	248	2.01
19	4,6,8-triethoxyoctan-2-one (diastereoisomer)	57.78	248	4.46
20	acetophenone	58.30	120	0.00
21	1,5,7-triethoxyheptan-3-one ?	71.35	246	2.03
22	4,6,8,10-tetraethoxydecan-2-one	74.87	332	2.71
23	4,6,8,10-tetraethoxydecan-2-one (diastereoisomer)	75.15	332	1.94
24	4,6,8,10-tetraethoxydecan-2-one (diastereoisomer)	75.36	332	4.82
25	4,6,8,10-tetraethoxydecan-2-one (diastereoisomer)	75.54	332	2.61
26	unknown	86.77		0.67

TABLE 3.1.4 (continued) *Compounds identified in the pyrogram of poly(vinyl ethyl ether) as shown in Figure 3.1.8.*

Peak	Compound	Ret. time	MW	Area %
27	unknown [73(100), 103(65), 98(23), 101(23, 145(17))]	86.94		0.70
28	unknown [73(100), 103(65), 98(23), 101(23, 145(17))]	87.10		0.42
29	unknown [73(100), 103(65), 98(23), 101(23, 145(17))]	87.65		0.87
30	unknown [73(100), 103(65), 98(23), 101(23, 145(17))]	87.81		0.71
31	4,6,8,10,12-pentaethoxydodecan-2-one	89.15	404	1.87
32	4,6,8,10,12-pentaethoxydodecan-2-one (diastereoisomer)	89.33	404	1.35
33	4,6,8,10,12-pentaethoxydodecan-2-one (diastereoisomer)	89.51	404	7.81
34	4,6,8,10,12-pentaethoxydodecan-2-one (diastereoisomer)	89.85	404	3.66
35	4,6,8,10,12,14-hexaethoxytetradecan-2-one	101.10	476	1.68
36	4,6,8,10,12,14-hexaethoxytetradecan-2-one (diastereoisomer)	101.21	476	1.02
37	4,6,8,10,12,14-hexaethoxytetradecan-2-one (diastereoisomer)	101.37	476	4.51
38	4,6,8,10,12,14-hexaethoxytetradecan-2-one (diastereoisomer)	101.49	476	2.40
39	4,6,8,10,12,14-hexaethoxytetradecan-2-one (diastereoisomer)	101.66	476	4.10
40	4,6,8,10,12,14-hexaethoxytetradecan-2-one (diastereoisomer)	101.81	476	1.64
41	4,6,8,10,12,14-hexaethoxytetradecan-2-one (diastereoisomer)	101.96	476	0.82
42	4,6,8,10,12,14,16-heptaethoxyhexadecan-2-one (diastereoisomer)	115.36	548	0.88
43	4,6,8,10,12,14,16-heptaethoxyhexadecan-2-one (diastereoisomer)	115.80	548	2.40
44	4,6,8,10,12,14,16-heptaethoxyhexadecan-2-one (diastereoisomer)	115.95	548	1.45
45	4,6,8,10,12,14,16-heptaethoxyhexadecan-2-one (diastereoisomer)	116.23	548	5.01
46	4,6,8,10,12,14,16-heptaethoxyhexadecan-2-one (diastereoisomer)	116.81	548	1.29

Although the pyrolysis and the separation of the pyrolysate were done using the same instrumental settings for 0.4 mg and for 0.8 mg samples, the pyrolysis of the larger sample forms significantly larger proportion of heavier fragment molecules, as can be seen in Figure 3.1.8. The ratio of the level of acetaldehyde (ret. time 5.89 min.) vs. that of ethanol (ret. time 12.41 min.) is about the same for the 0.4 mg sample and for 0.8 mg sample. However, the levels of these compounds and of many others are different. The differences are likely generated by the change in the temperature raise profile, and in the temperature distribution within the sample. Further discussion on pyrolysis of poly(vinyl ethyl ether) can be found in Section 5.5.3).

The change in sample size has been shown to influence product ratios, fractional conversions, and rates of pyrolysis for several polymers [14]. However, the dependence of pyrolysis results on sample size does not have only a negative impact on data reproducibility. This effect may reveal mechanistic features of the pyrolysis process, such as secondary reactions that occur during the residence time of primary products in the melt and diffusion-restriction of the interaction of long-chain radicals, when the thickness of the degrading film is comparable with the diameter of the hydrodynamic volume of the polymer molecules.

The reduction of sample size to a range over which any effects of sample size are eliminated may be related to other effects, some advantageous and some not. Secondary reactions during pyrolysis are diminished for a small sample, but the contact with metal surfaces may increase (relative to the amount of sample), which is not desirable because of possible catalytic effects. One determining factor that does not allow a significant decrease in the sample size is the limited sensitivity of the analytical procedure following pyrolysis. A sample that is too small may not be appropriate because the pyrolysis products cannot be properly detected. Also, the weight of a sample that is too small is difficult to measure with enough accuracy and precision. For

materials that are not homogeneous, the smaller the sample, the more difficult it is to obtain a representative sample. Restrictions to the choice of the sample size are also related to the losses due to the possibly incomplete transfer of the pyrolysate to the analytical instrument. This subject will be mentioned further as it relates to the analytical instrumentation attached to the pyrolyzer.

The actual temperature acquired by the sample during pyrolysis can be monitored using optical pyrometry or can be standardized between different pyrolyzers using a model compound. The procedure is based on the dependence of the composition of the pyrolysis products on temperature. One such compound chosen as a standard is an isoprene/styrene copolymer, trade name Kraton 1107 [15] (see Section 4.2).

The cooling of the sample from the T_{eq} value also may play a certain role in reproducibility, and the cooling may be related to THT. Some variability can be introduced if the pyrolysate is swept from the main heating source at different temperatures. At lower temperatures some condensation may take place in the pyrolyzer, affecting the analytical results. This problem is commonly avoided using appropriate heating of the pyrolyzer body (housing heating). The temperature of the housing is commonly maintained above the temperature of condensation of the components in the pyrolysate, which should be further analyzed. The heating of the pyrolyzer body, however, needs to be done such that the sample does not get heated before pyrolysis. When the sample is introduced in the pyrolyzer, there is commonly a waiting time before the sample gets pyrolyzed. For pyrolyzers with autosamplers, this waiting time can be quite significant. It is very important for reproducibility in analytical pyrolysis that the sample does not suffer modifications during this waiting time.

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3.2 INSTRUMENTATION USED FOR PYROLYSIS

- Resistively heated filament pyrolyzers

Resistively heated filament pyrolyzers have been used for a long time in polymer pyrolysis [1]. The principle of this type of pyrolyzer is that an electric current passing through a resistive conductor generates heat in accordance with Joule's law:

$$Q = I^2 R t = (V^2 t) / R \quad (3.2.1)$$

where Q is the amount of heat (in J), I is the current intensity (in A), R is the electrical resistance of the conductor (in Ohms), t is the time in sec and V is the voltage (in V). A simple flash pyrolysis unit that operates at a fixed voltage could easily be constructed. However, such a unit operating within common values for the current intensity and voltage will have a TRT that is too long to be appropriate for flash pyrolysis. Systems with boosted current or boosted voltage were used to achieve a more rapid heating [2]. These systems apply to the filament a constant current with an initial boost pulse to assure a rapid temperature increase at the beginning of the heating period. Values for TRT as low as 7 msec from ambient to 1000° C were reported for a filament pyrolyzer [3]. The ideal variation of temperature for a ribbon type filament heated at the maximum rate is illustrated in Figure 3.2.1.

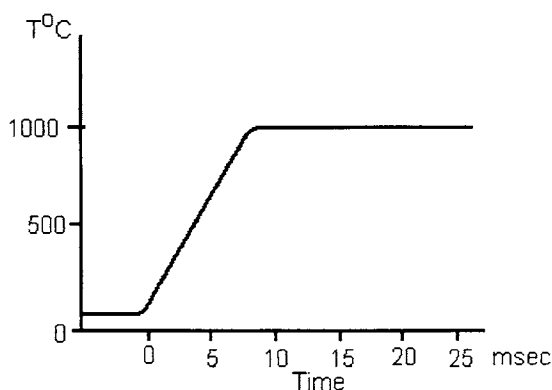


FIGURE 3.2.1. *Idealized temperature profile in time for a ribbon type filament heated at maximum rate.*

The true temperature of a sample heated using a filament pyrolyzer can be quite different from the above profile temperature, significantly lower temperatures being recorded inside the samples [4]. In order to obtain a correct T_{eq} , modern equipment uses a feedback controlled temperature system (see e.g. [5] for a more detailed description of this type of pyrolyzer). Several other procedures for a precise temperature control of the filament are available, such as the use of optical pyrometry or thermocouples [6, 7]. Special pyrolysis systems that allow programmed heated rates at different time intervals also are available [8].

The filament shape commonly used in resistively heated pyrolyzers is either a ribbon or a coil. The sample can be put directly on the filament or in a silica tube that fits in the

platinum coil. A silica (quartz) tube used as a sample container can be extremely useful in accommodating for pyrolysis of a wide variety of samples. However, when a silica tube is used, the TRT times are increased due to the larger mass that needs to be heated. The filament, the silica tube (if present), and the sample are maintained in a stream of inert gas and inside the heated housing of the pyrolyzer.

There are several advantages of the resistively heated filament pyrolyzers compared to other types. They can achieve very short TRT values, the temperature range is large, and T_{eq} can be set at any desired value in this range. Several commercially available instruments are capable of performing programmed pyrolysis, and autosampling capability is also available (such as the CDS AS-2500).

Some problems are inherent to this type of pyrolyzer. One such problem is that the set temperature and the actual temperature of the filament must be calibrated. The filament electrical resistance is part of the temperature controlling circuit. This resistance may modify in time, mainly in the systems where the sample is put directly on the filament. Because of this, the correspondence between the set operating temperature and the actual temperature will change during the life of the filament. Even in correctly operating instruments, problems may occur in achieving the T_{eq} as precisely as the manufacturer may indicate [9].

Another problem with filament pyrolyzers is the possibility that the filament may be non-uniformly heated over its length. This may determine different T_{eq} 's in different points of the filament. If the sample is not always placed in the same point of the filament in repeated experiments, this may introduce a rather drastic reproducibility problem. In spite of these disadvantages, the resistively heated filament pyrolyzers are among the most common ones, and very good reproducibility frequently has been reported.

- Curie point pyrolyzers

Ferromagnetic conductors can be rapidly heated by interaction with a high frequency (radio frequency, RF) electromagnetic field. The sample to be pyrolyzed can be placed in close contact with the conductor, which can be shaped into different forms such as a wire, ribbon, folded ribbon, or cylinder to properly hold the sample. The heating of the conductor and subsequently of the sample can be realized with a short TRT, commonly between 10 and 100 ms. Eddy currents in the conductor surface (skin) and hysteresis losses due to changes in the magnetic polarity cause the temperature to increase rapidly when the conductor is placed in the high frequency electromagnetic field. The increase in temperature is, however, limited for these ferromagnetic conductors to the Curie point temperature [10]. This is a temperature specific for each material where the transition from ferromagnetic to paramagnetic properties occurs. In this way, besides a rapid heating, a well-defined end temperature is attained. This end temperature (Curie point) depends on the composition of the ferromagnetic metal or alloy. Table 3.2.1 gives the Curie point temperatures for several Fe/Ni/Co alloys.

TABLE 3.2.1. *Curie points of several ferromagnetic alloys.*

Fe %	Ni %	Co %	Curie point temp. °C
0.0	100	0.0	358
61.7	0.0	38.3	400
55.0	45.0	0.0	400
50.6	49.4	0.0	510
40.0	60.0	0.0	590
42.0	41.0	16.0	600
29.2	70.8	0.0	610
33.3	33.3	33.4	700
100.0	0.0	0.0	770
0.0	55.0	45.0	800
0.0	40.0	60.0	900
0.0	0.0	100.0	1128

As seen in Table 3.2.1, temperatures in a wide range can be obtained using different compositions for the ferromagnetic alloy. However, the temperatures obtained with Curie point instruments cannot be varied continuously.

Commonly used RF frequencies in Curie point pyrolyzers are 400 to 1000 kHz, and the power outputs range from 100 to 1500 watts. The rate of temperature rise depends on the conductor mass and specific heat, as well as on the power consumption of the ferromagnetic conductor. This power consumption per unit surface is related to the amount of heat generated by the conductor and implicitly to the temperature. More detailed descriptions of the parameters implicated in the heating of a ferromagnetic conductor located inside a high frequency induction coil are found in literature [5, 10].

Different practical constructions of a Curie point pyrolyzer are commercially available. In these systems, the sample is put in direct contact with the ferromagnetic alloy, which is usually in the shape of a ribbon that can be folded over the sample forming a sample holder. The sample and its holder are maintained in a stream of inert gas in a similar way as for resistively heated filaments. The housing where the sample and its ferromagnetic holder are introduced is also heated to avoid the condensation of the pyrolysate but without decomposing the sample before pyrolysis. Autosample capabilities for Curie point pyrolyzers are also commercially available (e.g. DyChrom model JPS-330) [11, 12].

The Curie point pyrolyzers have several advantages when compared to other systems. The TRT is usually short and the heating rate is reproducible. The T_{eq} temperature is accurately reproducible for the same alloy. The contact between the sample and the heated alloy is good, which assures that the heat transfer to the sample is rapid and uniform. On the other hand, the set temperatures can be only discrete and are limited to the values offered by different alloys. Even though the direct contact of the sample with the ferromagnetic alloy offers the advantage of a good heat transfer, it can be a source of catalytic interferences. For this reason some suppliers offer gold plated ferromagnetic sample holders.

- Furnace pyrolyzers

Furnace pyrolyzers are devices used in both flash pyrolysis and slow gradient pyrolysis. For flash pyrolysis, the common principle of use is to keep the furnace at the desired temperature and to suddenly introduce the sample into the furnace. The heating of the furnace is commonly done using electrical heating, which can be controlled using thermocouples and feedback systems to maintain the correct temperature. An inert gas flow is commonly passed through the furnace to sweep the pyrolysis products into the analytical instrument. For analytical purposes it is, therefore, preferable to have small furnaces with low dead volumes, such that the gas flow can be kept at relatively low values. On the other hand, if the mass of the furnace is small, the sample introduction may modify the furnace temperature. Several designs were used for furnace pyrolyzers, a successful one being a vertical furnace that allows the sample to be dropped from a cool zone into a heated zone (e.g. the SGE microfurnace Pyrojector) [13].

A factor that must be considered with furnace pyrolyzers as well as with the other types of pyrolyzers is the achieving of short TRT values. A slow sample introduction in the hot zone of the furnace will end in a long TRT. A poor contact between the sample and the hot source may also lead to long TRT, most of the heat being transferred by radiation and convection and not by conduction. However, fairly short TRTs in furnace pyrolyzers were reported in literature [14, 15]. Also, in furnace pyrolyzers it is more common to see differences in the temperature between the furnace and the sample. Due to the poor contact between the sample and the hot source, the sample may reach a lower actual temperature than the temperature of the furnace wall. This may be the explanation why there were reported variations in the pyrolysis products in microfurnace systems as compared to the results obtained in inductively or filament heated pyrolyzers [16, 17]. As an example, in the study done on Kraton 1107 [16], the decomposition was found linear for the oven temperature and the ratio of two monomers (styrene and dipentene) only in a temperature range from 450° C to 625° C, which is narrower compared to that found for a filament or Curie point pyrolyzer.

This type of pyrolyzer is used successfully when larger amounts of sample need to be analyzed. This is a common case for the pyrolysis of non-homogeneous samples when a few mg of sample do not represent well the average sample composition, or when a large amount of pyrolysate must be generated in order to analyze specific trace components. Slow gradient pyrolysis (at programmed rates) can easily be performed with furnace pyrolyzers, but rapid programmed heating is more difficult to achieve. A system using a PTV (Programmable Temperature Vaporization) injector has been reported [18] as being used successfully for programmed heating in two different steps, one at 200° C and another at 450° C. The heating gradient was, however, not faster than 8° C/ s. Slow gradient temperatures are commonly used in a series of thermal analysis instruments that are equipped with programmable furnaces. However, these thermoanalytical techniques are sometimes classified separately from pyrolysis as previously indicated.

Other different models of furnace pyrolyzers were reported in literature [12]. As an example, a two-temperature zone furnace was made, and it was utilized to provide information about more volatile compounds trapped (adsorbed) in a sample as well as for performing true pyrolysis. In this system, the sample is heated first at 300° C where the volatile compounds are eliminated, and then the sample is pyrolyzed at 550° C.

Sealed vessel pyrolysis is another pyrolysis type that is performed in furnace type pyrolyzers. In this type of pyrolysis, the sample is heated for a relatively long period of time, in a sealed vessel, generally at relatively low temperature (below 350° C). The pyrolysis products are further analyzed, commonly by off-line procedures (GC, GC/MS, FTIR, etc.) The technique allows the pyrolysis to be performed for as long as months and to use different atmospheres (inert or reactive) [19]. The procedure is not used only as an analytical tool, and it can be seen as a preparative pyrolysis technique.

- Radiative heating (laser) pyrolyzers

Laser pyrolyzers are practically the only type of radiative heating pyrolyzer with certain applicability. Attempts were made in the past to use a strong light/heat source and focus the beam with lenses [20] to achieve the desired power output. However, the laser as a radiative energy source is much more convenient. The laser beam can be focused onto a small spot of a sample to deliver the radiative energy. This provides a special way to pyrolyze only a small portion of a sample. A variety of laser types were used for pyrolysis purposes: normal pulsed, Q-switched, or continuous wave (cw) [21], at different energy levels. More common are the normal pulsed high-power lasers. Some instruments use condensing lenses to enhance the energy delivered to a small area of the sample.

A range of energies can be transferred to the sample by the laser. For a spot of about 1 mm diameter, a typical pulsed laser used for pyrolysis can generate a mean power density of 0.2–2.0 MW/(cm²). This high energy is partly absorbed by the sample, and a rapid volatilization and decomposition take place. A plume is commonly generated along the axis of the beam, and more radiative energy is absorbed in this plume.

The theory of thermal aspects of laser desorption has been developed for a substrate surface subjected to pulsed laser irradiation, assuming that the laser intensity has a Gaussian distribution [22]. The given surface is covered with the organic layer, which does not absorb the laser energy. However, the heat flux in the substrate that absorbs the energy heats the sample to the same temperature as the substrate. The temperature of the plume may rise fairly high, and values as high as 10,000° C were reported. However, more reasonable values range from 500° C to 2000° C. At temperatures as high as 2000° C, only some stable radicals will exist. Therefore, the part of the sample taken into the plume will generate after cooling only non-characteristic small molecules such as acetylene. The free radicals in the plume may produce unexpected secondary reactions. However, enough heat is transmitted by the hot plasma around the focus point of the laser. This heat will produce pyrolysis products similar to those generated by other pyrolysis techniques. Some secondary reactions may take place between these pyrolysis products and the free radicals from the plume.

The maximum energy of the laser can be higher than needed for the pyrolysis purposes and needs to be attenuated. For a cw laser with a nominal energy of 100 W, the output has to be attenuated by operating the laser at about 10 W and by splitting the beam. Figure 3.2.2 shows simplified diagrams of two laser micropyrolysis setups. The first apparatus is used with a cw laser. A microscope allows the inspection of the area to be analyzed and the focusing of the beam on the portion of interest on the sample. The laser beam is also split (and attenuated) in the microscope by using a semitransparent mirror, which allows control of the percent of the beam intensity that reaches the sample

(5–15%). For a cw laser, powers between 0.5 to 5 W with exposures varying from 1 s up to 5 min. were utilized for pyrolysis. The surface of the area exposed to the laser was also varied from $20\ \mu\text{m}^2$ to $400\ \mu\text{m}^2$.

The second apparatus uses a pulsed laser (pulse energy of about 1 joule) and an alignment laser. In order to direct the high energy laser beam to the right place on the sample, some commercially available pulsed laser pyrolyzers have a low energy laser, or “alignment” laser, which allows the selection of the desired spot on the sample to perform the pyrolysis.

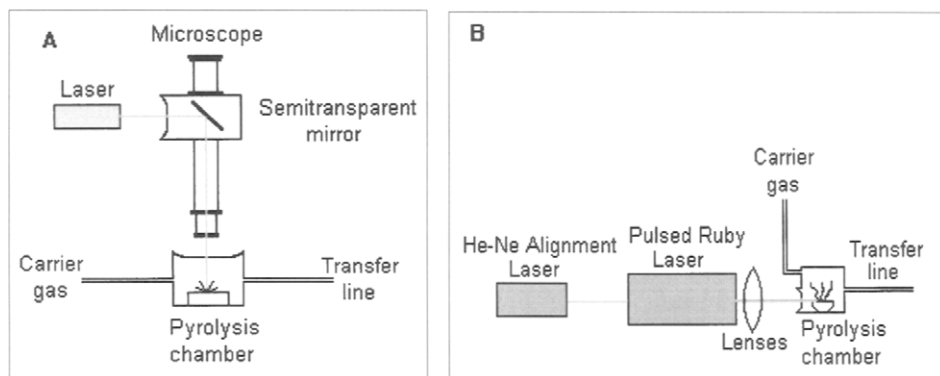


FIGURE 3.2.2. Simplified diagrams of two laser micropyrolysis setups: **A** cw laser with a microscope, **B** pulse laser with alignment low power laser.

Besides the formation of some unusual products due to secondary reactions, there are several other problems regarding the use of lasers as an energy source for pyrolysis. A first problem is related to the absorption of the radiative energy into the sample. Transparent samples do not absorb the radiative energy properly. For this reason, several procedures were utilized to make the sample more opaque. One such procedure consists of adding into the sample powdered graphite [23] or a metal powder such as nickel [24]. This addition can, however, modify the course of the pyrolysis by catalytic effects or side reactions. A different procedure consists of depositing the sample in a very thin layer on a support that absorbs the radiation generating heat. In particular, a blue cobalt-glass rod has been used [24] as a support for the sample, with temperatures attaining 900–1200° C.

Another typical property of the laser pyrolysis is that it can achieve very short TRT times and also very short cooling times, in the range of 100 to 300 μs . This will contribute to the uniqueness of the degradation conditions for the laser pyrolysis, which are rather different from the other types. In addition to this, the capability to pyrolyze only a very small area of the sample is characteristic for most laser pyrolyzers. This directional nature can be of exceptional utility when combined with the microscopic inspection of a particular sample. Inclusions and inhomogeneities in the samples, etc. can be analyzed successfully using this technique.

On the other hand, deliberate defocusing of the laser beam also was experimented [25] in order to cover a wider area on the sample for performing pyrolysis. Several

alternative approaches also were examined in order to provide more detailed information on polymers. For the study of the order of formation of specific molecular fragments during thermal degradation, for example, a time-resolved laser-induced degradation was applied [26]. Also, attempts were made to use specific wavelengths corresponding to a given vibration of the molecule in order to break specific bonds, using lasers as a source of energy.

A problem with lasers is the difficulty of knowing precisely the equivalent temperature of pyrolysis. Also, due to some inherent characteristics of laser pyrolysis, its reproducibility is not always high. Several studies [27] showed variability in the total mass of material pyrolyzed and difficulties in the control of the pyrolysis temperature. The secondary reactions with the radicals from the plume (although catalytic reactions are probably absent) also make this technique less reproducible. More recently, considerable effort was put into improving the reproducibility of the use of laser techniques for pyrolysis. For example, a UV laser pyrolysis coupled with a fast gas chromatography/time-of-flight mass spectrometry analytical procedure has been developed for the rapid characterization of synthetic polymers [28, 29]. This instrument combines a Q-switched Nd:YAG laser, frequency quadrupled to 266 nm, with fast gas chromatography/time-of-flight mass spectrometry (GC/TOF-MS). The combined instrument integrates the processes of sampling by the laser, reconcentration of the volatile products, and sample introduction to the GC/TOF-MS. This method uses a UV laser as a fragmentation source, which can create pyrolysis fragments without prior sample pretreatment, even with transparent organic materials. Gaseous pyrolysis products are then concentrated on a cryogenic trap cooled by liquid carbon dioxide and thermally desorbed into the head of the chromatographic column for separation and identification of the components by GC/TOF-MS. Interfacing laser pyrolysis to fast GC/TOF-MS reduces overall analysis time without compromising the chromatographic peak information. By proper tuning of the experimental variables of this type of instrument so that both low and high molecular pyrolysis products are transferred to the GC/TOF-MS, the analysis system can be efficient and reproducible.

Besides conventional laser pyrolysis, several other techniques evolved around the concept of evaporating the sample using a laser beam. However, most of these techniques were developed with the purpose of preserving the structure of the analyte while transferring it into an ionized gas form. Techniques such as MALDI (matrix assisted laser desorption/ionization) [30–33] are commonly used for the analysis of biopolymers. However, MALDI does not (or is not intended to) produce pyrolysis of the analytes and cannot be classified as a pyrolytic technique.

- Pyrolyzers with gas switching capability and/or with concentrators

Gas switching capability is a useful feature for a pyrolyzer. Pyrolysis in specific gases that are different from helium is important in a number of practical applications. One of these is the study of burning. Burning is a complex process, mainly in the case of solid samples. It may include a combustion component, pyrolysis, and several physical processes such as melting, distillation/volatilization, and entrainment of solid particles. Combustion is an oxidation process that generates compounds such as CO₂, H₂O, CO, N₂, and also produces heat (combustion and burning are sometimes used interchangeably, but it is preferable to make a distinction between these terms). The

heat from combustion can produce pyrolysis, which can be either an exothermic or an endothermic process. Pyrolysis during burning may take place without the influence of oxygen. Some burning processes even generate reducing gases such as CO, and pyrolysis may be considered as taking place in a reducing atmosphere. However, it is common during burning that the associated pyrolysis takes place in the presence of some oxygen. For this reason pyrolysis in a mixture of inert gases such as He or N₂ with a certain proportion of O₂ is a common type of study. Many organic compounds heated in air at the temperatures used for pyrolysis (500–600° C) will ignite, leading to combustion. However, for a variety of samples it is possible to perform true pyrolysis without the ignition of the sample in a mixture of an inert gas and a smaller content of oxygen (compared to air), such as 2–5%.

The presence of oxygen in the gas used for pyrolysis can be a problem when the process is performed on-line with an analytical technique such as GC or GC/MS. Chromatographic columns are typically sensitive to the presence of oxygen, and traces of oxygen are undesirable in a mass spectrometer. For these reasons, the pyrolyzers equipped to perform pyrolysis in a gas other than He or H₂, which are typical carrier gases in GC (or GC/MS), have a gas switching capability. These instruments have a source of carrier gas, and another one for the pyrolysis gas. There are practically two types of instruments that allow gas switching. The first type of instrument uses a valve system to switch the gas in the pyrolyzer between the carrier gas to the pyrolysis gas, and vice versa. Since in most cases the instruments are used on-line, when the carrier gas is replaced in the pyrolyzer with another gas, this gas also makes its way into the GC. The system does not protect the GC column from a surge of oxygen content when, for example, the pyrolysis gas contains oxygen. However, the gas flowing through the system is replaced with the carrier gas immediately after the pyrolysis, and the surge of oxygen in the GC is temporary and not significant. Excellent results can be obtained using this simple system, with no significant problems for the GC column.

A different system uses a complete replacement of the pyrolysis gas with the carrier gas before the pyrolysate is sent into the GC system. For attaining this goal, such a system uses a trapping material for the pyrolysate. Typical chromatographic stationary phases or materials with application in gas collection are used for this purpose (see e.g. [34]). Among the more common trap phases are Tenax® (poly-2,6-diphenyl-*p*-phenylene oxide) and porous poly(styrene-*co*-divinylbenzene), known as Chromosorb®, Amberlite XAD, and Porapak®. The typical scheme of this type of pyrolyzer is shown in Figure 3.2.3. The pyrolyzer works in two stages. In the first stage, pyrolysis is done in a selected gas for pyrolysis and is adsorbed in a trap at room temperature on a stationary phase. Meanwhile the carrier gas flows directly to the GC or GC/MS system. In the second stage, the six-port valve is switched, and the carrier gas flows through the trap. The pyrolysate is desorbed from the trap by heating. The carrier gas transfers the pyrolysate into the GC system. This procedure also can be used for the preconcentration of a sample if this is necessary. If the trap material is correctly selected and the heating of the trap for the desorption is done rapidly, the system does not require a cryofocusing step. All transfer lines must be heated to avoid condensation.

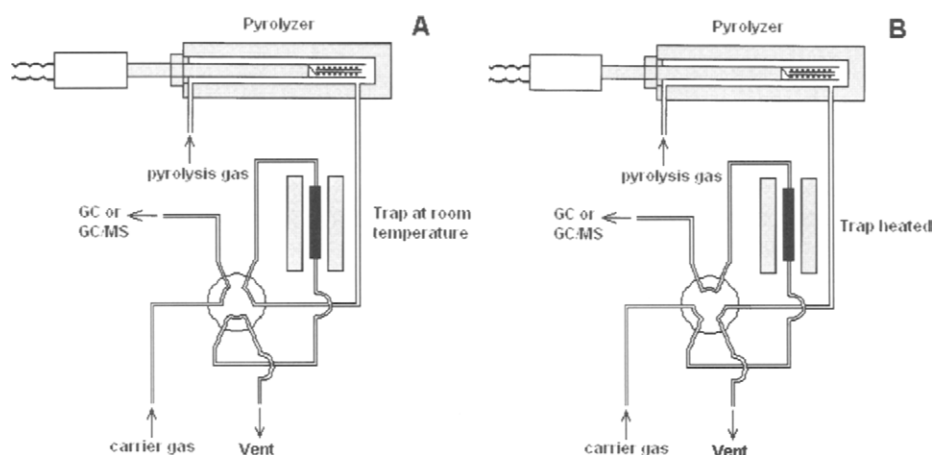


FIGURE 3.2.3. *Schematics of a pyrolysis system that allows gas switching and pyrolysate trapping.* In stage A, pyrolysis is done in a gas selected for pyrolysis and the pyrolysate is adsorbed in a trap at room temperature on a stationary phase. In stage B, the carrier gas is switched through the trap, which is desorbed by heating.

Both systems, the one without trapping and the one with trapping, have advantages and disadvantages. The first procedure is simpler and more robust, but does not eliminate completely the pyrolysis gas from the analytical instrument. The second system is more complicated, requiring a number of heating zones in order to avoid condensation and carryover problems. The stationary phase used to collect the pyrolysate may be selective and may retain only a part of the pyrolysis products. Other pyrolysate components may be retained permanently and remain in the trap. On the other hand, this system completely eliminates the pyrolysis gas from the analytical instrument, allows preconcentration if necessary, and the selectivity of the adsorbing phase can be used in the favor of the analysis by enhancing the detection of specific components.

Concentration techniques in GC are used mainly for trace analysis. Pyrolysis commonly generates enough material for a GC analysis even when a very small amount of sample is taken for analysis. For this reason, concentration techniques are not frequently associated with Py-GC. However, for the analysis of specific traces in pyrolysates, the amount of material generated from a small sample is not always large enough. In these cases, it is more common to use pyrolyzers with larger sample capacity (such as furnace pyrolyzers) followed by the off-line processing of the pyrolysate.

- Other pyrolyzer types

Besides the previously described pyrolyzer types, some other pyrolyzers have been constructed and reported in literature [14, 35, 36]. Some are based on variations of typical pyrolyzer systems. One such system uses a microfurnace pyrolyzer with the capability to hydrogenate the pyrolysis products. For this purpose, the system uses hydrogen carrier, and, in line with the microfurnace, it has a catalyst column containing a

solid support with Pt-catalyst (and a precolumn portion to trap nonvolatile pyrolysis products) [37].

A different system utilizes as a source of heat an electric arc [50], but limited applications were reported for it, and also an infrared pyrolyzer is manufactured [49]. Other techniques, such as photolysis [38], were utilized for breaking down polymers for further analysis. However, these cannot be considered pyrolytic procedures. A theoretical approach has been developed [38] to compare mass spectrometric, thermolytic and photolytic fragmentation reactions.

Other alternative techniques for performing pyrolysis are described in literature. An example is the in column pyrolysis [39], where pyrolysis is carried out in a segment of deactivated stainless steel tubing inserted between the injection port of the GC and the analytical column. The procedure assures that all pyrolysis products that can go through the chromatographic column are analyzed, and no losses by condensation take place, for example in the housing of the pyrolyzer. One disadvantage of this technique is that each sample loading is done on a replaceable piece of steel tubing, which must be mounted and dismounted in the gas chromatograph for each sample.

One other pyrolytic technique used for polymer analysis is pyrolysis-fractography [40]. In this technique, the pyrolysate is generated when the polymer is instantaneously pyrolyzed at 600 °C, similarly to other flash pyrolysis techniques. However, the pyrolysate is introduced together with the carrier gas into a short length of deactivated stainless steel capillary tube situated in the gas chromatographic oven. By a programmed heating, the oven temperature is linearly raised so that the pyrolysates are fractionated, and a fractogram is obtained using for detection a mass spectrometer or a flame ionization detector. Studies on polyethylene, polyurethane, and melamine formaldehyde resin were performed using this technique.

- Comparison of analytical performances of different pyrolyzer types

Comparisons between the results obtained using different pyrolyzers are not uncommon in literature [14, 41–43]. These comparisons have two objectives: to assess the quality of the analytical results (reproducibility, sensitivity, etc.) of a certain type of pyrolyzer and to indicate how the results of one pyrolyzer can be compared to those of another type.

The comparison is not always straightforward because the analytical instrument at the end of the pyrolyzer may play an important role regarding the quality of the data. Table 3.2.2 gives a global view of different characteristics of the main pyrolyzer types.

TABLE 3.2.2. *Comparison of the main characteristics of several pyrolyzers.*

Property	Curie point	Heated filament	Micro furnace	Laser
Temperature limit °C	1128	1100	1500	high
Temperature control	discrete	continuous	continuous	uncontrolled
Use of temp. gradients	not possible	possible	common	possible
Minimum TRT	70 ms	10 ms	0.2s - 1 min	10 µs
Sample size µg	10 - 1000	10 - 1000	50 - 5,000	20 - 500
Reproducibility	very good	very good	good	poor
Catalytic reactions	some	low	low	very low
Use with analytical instruments	on-line/off line	on-line/off line	on-line/off line	on-line/off line

The reproducibility of the results for heated filament pyrolyzers and Curie point pyrolyzers as well as the comparison between the two systems was reported for a number of materials [41]. The reproducibility of the analysis was evaluated both qualitatively and quantitatively. It was found that for most samples the results are obtained with very good reproducibility for the same instrument. However, differences in the instrumentation may play an important role regarding the dissimilarity of the results, even when they are operated at comparable parameters. These differences are typically less pronounced between filament pyrolyzers and Curie point pyrolyzers. Also, microfurnace pyrolyzers are closer to filament pyrolyzers than large furnace ones. On the other hand, laser micropyrolyzers or sealed vessel furnace pyrolyzers may lead to quite different results.

Equal in importance to the temperature control characteristics are the heat transfer parameters from the heating element itself or from the probe housing, etc. The dead volumes, the gas flow through the pyrolyzer, the amount of pyrolysate that reaches the analytical instrument, etc. also may play a role in the pyrolysis outcome.

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3.3 INSTRUMENTATION APPLIED FOR THE ANALYSIS OF PYROLYSATES

- General aspects

Pyrolysis products generated by the pyrolyzer can be analyzed either on-line or off-line using an analytical instrument. Gas chromatography (GC) and gas chromatography-mass spectrometry (GC/MS) are the most common techniques utilized for this purpose. The typical chemical complexity of pyrolysates requires for the analysis an efficient separation, and that explains the common use of chromatography coupled with the analytical pyrolysis. Since low molecular mass fragments are frequently generated in the pyrolytic process, GC is the technique usually applied for the separation. The use of MS as the detection tool provides, besides the identification capability, very good sensitivity. This sensitivity is necessary, mainly because the amount of sample used in analytical pyrolysis is very small (up to a few mg). The analysis of trace components in pyrolysates is also possible using only a very sensitive detection as that offered by MS. The qualities of Py-GC/MS make this technique the most convenient and widely utilized in practice.

The use of Py-GC/MS has, nevertheless, some disadvantages. Larger molecules generated as fragments from polymers are not easily detected and analyzed by this technique, and they may contain valuable structural information. Also, for a complete analysis of the pyrolysates, the compounds associated with the char sometimes should be analyzed. These nonvolatile components are not transferred in a gas flow. For this reason, the use of Py-GC/MS may leave unsolved a series of structural problems. HPLC was sometimes utilized for the separation of larger compounds from pyrolysates. However, liquid chromatography, even coupled with MS does not provide enough identification capability (unless a LC/MS/MS system is used) since very little fragmentation is generated in LC/MS, and the identification of the molecular species in pyrolysates is less successful. Other techniques such as FTIR or even NMR can be utilized for the analysis of pyrolysates, but their lower sensitivity compared to mass spectrometry explains their limited usage.

- On-line pyrolysis-GC and pyrolysis-GC/MS

In on-line pyrolysis-gas chromatography (Py-GC) or on-line pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS), the housing of the pyrolyzer is directly connected to a GC. This can be done using a short tubing (properly heated to avoid condensations) connected to the injection port of the GC instrument or using a piece of deactivated silica capillary column with one end in the pyrolyzer housing passing through the injection port of the GC and connected directly to the analytical GC column. A scheme (not to scale) of such connections is shown in Figure 3.3.1 (see e.g. [1]). Some details regarding the gas flow control are also shown in the figure. Other instrumental settings are possible.

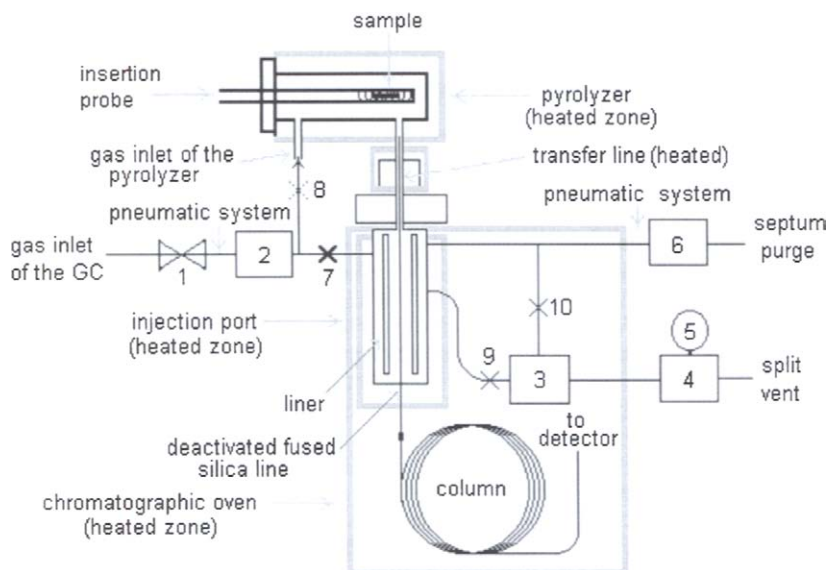


FIGURE 3.3.1. *Simplified diagram of a Py-GC system (not to scale). (See text for explanations).*

In Figure 3.3.1 the pyrolyzer is schematized as a heated filament type. A piece of a deactivated fused silica line is passed through the injection port of the GC and goes directly into the pyrolyzer. This piece of fused silica is connected to the column, which is placed in the GC oven. The pneumatic system exemplified in the figure consists of (1) a mass flow controller, (2) an electronic flow sensor, (3) a solenoid valve, (4) a back pressure regulator, (5) a pressure gauge, and (6) septum purge controller. The connection (7) is closed when working in Py-GC mode, and connection (8) is open. Connection (7) is open when the system works as a GC only. Connection (9) is closed and connection (10) is open when the GC works in splitless mode (purge off). Connection (10) is closed and connection (9) is open when the GC works in split mode (purge on). No details on the GC oven or on the detector are given in Figure 3.3.1. More complicated Py-GC systems are available. One such system includes a cryofocusing trap between the injection port assembly and the chromatographic column.

This trap is not used in typical flash pyrolysis experiments. However, if the pyrolysate is generated for a longer period of time, and it is not delivered to the chromatographic column similarly to a typical injection, a cryofocusing attachment is necessary. In principle, this consists of a short tube through which passes a capillary transfer line (or part of the column). The cryofocusing tube can be cooled at subambient temperatures for a determined period of time and condenses the sample injected in the GC. At the start of the GC run, the cryofocusing tube can be rapidly heated to evaporate the condensate.

Even when they have some volatility, higher boiling point compounds are sometimes difficult to transfer after being generated from the sample, since they have the tendency to condense on cooler surfaces. For this reason, proper heating of the pyrolyzer housing and of the transfer line are necessary. On the other hand, in case of thermally sensitive samples, uncontrolled thermal decomposition must be avoided before the true pyrolysis. This is possible when the sample is introduced in the pyrolyzer housing before the pyrolysis and the walls of the housing are too hot. Also, the temperature of the pyrolyzer housing and of the transfer lines should not exceed that of the GC oven since compounds with high boiling points should not accumulate at the beginning of the chromatographic column. The reproducibility of Py-GC/MS is typically very good. Some care must be taken regarding the control of the pyrolysis process as well as in maintaining good chromatographic practices. The only possible disadvantage of this technique is the relatively long time required for the GC separation (which can reach several hours) unless fast chromatographic procedures are applied. Some variability can be encountered in Py-GC/MS due to the variability in the polymer structure and/or composition, which can generate different pyrograms for nominally the same type of polymer.

The sample size and the flow of gas used in the pyrolyzer should match the requirements imposed by the GC system. For this reason, the analytical pyrolyzers are constructed such that there are no significant discrepancies with the GC requirements. Since pyrolysis is commonly performed in a flow of an inert gas, this is typically used as the carrier gas for the chromatography. For specific needs, pyrolyzers can have the capability to perform pyrolysis in a different gas from the carrier gas, and in these cases a gas exchange is needed between the pyrolyzer and the GC (see Section 3.2).

The shape and size of joining elements between the pyrolyzer and the GC influence the dead volumes encountered by the analytes affecting the efficiency of separation. These dead volumes should be kept as small as possible, and for Curie point and filament pyrolyzers this task is readily achieved. However, for microfurnace pyrolyzers, the gas flow and dead volumes may raise some problems [2]. Some special transfer capabilities for the pyrolysate were reported with improved results regarding the transfer, for example using a system similar to that of an "on-column" injector employed to separate high-boiling compounds [3]. In-column pyrolysis [4] also avoids any additional dead volumes in pyrolysate transfer.

In some instances it is necessary to analyze both the volatile compounds that are generated at mild heating of the polymer (sometimes below 100° C) and also the typical pyrolysis products. Several two-step (or multi-step) experiments were reported [5] that allow this type of analysis. For the analysis of traces of volatile materials, purge-and-

trap is a common procedure. It consists of purging the sample (heated at a given temperature usually below 100° C) with an inert gas and passing the purging gas over a solid-phase adsorbent. After a certain purging period, the sorbent is desorbed by heating. Following the first step desorption, a true pyrolysis step follows. The pyrolysates may or may not be passed through the adsorbing trap. Some compounds with higher boiling points or polarity may be irreversibly adsorbed in traps.

The complex nature of pyrolysates requires in some situations a better separation of the components than commonly possible using standard chromatography. For a better separation, the peaks from a given interval in the first chromatogram can be subjected to a second separation. Bidimensional gas chromatography was developed with the purpose to address this problem of the separation of complex mixtures [6]. The technique allows a small portion to be cut from a chromatographic separation and be sent to a second chromatographic column for additional separation. This process can be accomplished in different instrumental setups (see e.g. [1]). Comprehensive chromatography is a promising alternative for separation of complex pyrolysates [7, 8].

Following the separation of pyrolysates, the detection can be done using common procedures for GC such as thermal conductivity detection, flame ionization detection (FID), etc. However, nonselective detectors without the identification capability are less common than mass spectrometric detection. While a GC separation with FID detection can provide only a fingerprint chromatogram for a specific polymer pyrolysate, mass spectrometry allows, at least in principle, the identification of pyrolysate components. The chromatographic separation being highly dependent on the nature of the GC column (nature of stationary phase, physical dimensions of the column, etc.) and the separation conditions, only by maintaining these parameters constant can similar chromatograms be obtained for the same pyrolysate/polymer. This imposes restrictive utility of such fingerprint chromatograms. On the other hand, the identification of pyrolysate composition using for example Py-GC/MS is a powerful tool for polymer identification, as well as for the detection of other related information such as the presence and nature of plasticizers, antioxidants, impurities, etc. Since larger molecules tend to decompose at typical pyrolysis temperatures (500–800° C), many components in the pyrolysates have relatively high volatility, and GC/MS analysis is readily feasible.

The result of a Py-GC/MS analysis is a chromatogram of the pyrolysate, commonly indicated as a *pyrogram*. Py-GC/MS can be used as an analytical tool in different manners. One is the identification of as many compounds as possible in the pyrogram. This is usually done with the purpose of understanding the type of chemicals released during pyrolysis, for example for purposes related to health or environmental issues. For polymer identification, not all the components in a pyrolysate need necessarily be determined, since some small molecules in the pyrolysate are diagnostic for a polymer identification. For example, the detection of 4-chlorostyrene in the pyrolysate of a polymer is a strong indication that the polymer is, or contains, poly(4-chlorostyrene). In other cases, when significant levels of monomer or of a unique compound are not generated during pyrolysis, the use of a marker compound for the identification of a polymer is more difficult. Also, in the case of copolymers with only a small amount of one of the comonomers present, a thorough pyrolysate analysis may be necessary for the detection of this comonomer. Some applications involve the use of a whole pyrogram, either obtained by Py-GC or by Py-GC/MS, as a fingerprint for the polymer.

This technique is very useful when the instrumental conditions are not changed and the same set of samples is analyzed, for example, for quality control.

A number of technical details are associated with Py-GC/MS, some related to the separation process in the gas chromatograph and others related to the mass spectral detection. The chromatographic separation should be done such that the components from the pyrolysate are well differentiated, and the heavier compounds that are more difficult to elute from the chromatographic column are not left there. These conditions are somewhat opposing each other since a column with more theoretical plates and possibly more polar is very useful for a good separation, while a shorter column and resilient to heating at higher temperatures is necessary to completely elute the pyrolysate from the column. The stationary phase of the chromatographic column (typically a capillary column) is critical for good separations. The most common stationary phases are poly(dimethylsiloxane) with various trade names (DB1, Equity -1, HP-1 ZB-1, etc.), poly(dimethylsiloxane) + 5% poly(diphenylsiloxane) with various trade names (DB5, Equity-5, SPB-5, HP5, Rtx-5, etc.), and poly(ethylene glycol) with various trade names (DB-Wax, Carbowax, Supelcowax 10, ZB-Wax, etc.). However, many more types of stationary phases are available and can be used for pyrolysate separation. Other characteristics for the chromatographic column such as length, internal diameter, stationary phase film thickness, etc. have to be properly selected for an optimum separation. The identification of all pyrolysate components is not usually possible since the GC/MS allows only the analysis of the more volatile portion of the pyrolysate. If the window of compounds seen by GC/MS is diagnostic for the polymer, no further analysis is necessary when only this is the purpose of the analysis. In some instances the pyrolysis study is done for the identification of all the components. In this case further analysis may be necessary involving for example derivatization of the pyrolysate or the use of HPLC. Also, more advanced analytical procedures can be used such as GC/MS/MS.

The selection of mass spectrometer parameters is another important feature for a successful analysis. Typically, the MS instrument is operated in positive electron impact (EI⁺) ionization mode with the electron energy at 70 eV, and with ion collection in a range of m/z starting around 15 and up to 1000. Narrower ranges are very common since the increase in the mass of the analyte beyond 500–600 a.u. is associated with a lack of volatility. Once the mixture of compounds from the pyrolysate is separated by GC, the fragmentation pattern from each molecule is used for chemical identification. Once the molecules are identified, for higher sensitivity of the mass spectrometer it is possible to use single ion monitoring (SIM), which can be useful mainly when a particular trace component is searched for in the pyrolysate. Other ionization modes such as chemical ionization (CI) with methane, butane, or ammonia as a reagent gas and other mild ionization techniques are sometimes beneficial for pyrolysate analysis. These techniques are particularly used in pyrolysis-mass spectrometry, and they avoid further fragmentation typical in EI⁺ ionization, providing information only on the molecular ions of the compounds in pyrolysates. Since pyrolysates are frequently complex mixtures, continuous effort has been invested and is reported in literature for the simplification of the signal generated by the MS instrument and for allowing identifications from one single composite spectrum. For this reason some studies of the pyrolysate have been performed using Py-MS/MS techniques. A more elaborate

description of various analytical pyrolysis techniques can be found in other published materials (see e.g. [1, 5, 9]).

- On-line pyrolysis-MS

In pyrolysis-mass spectrometry (Py-MS) the pyrolysate is directly transferred to a mass spectrometer and analyzed, generating a complex spectrum. The sample introduction can be done using various techniques. One simple technique is the direct insertion probe (DIP) where the sample is deposited on an insert that has the capability of heating the sample and of introducing the pyrolysate directly into the ion source of the mass spectrometer (see e.g. [1]). Another technique is the Curie point Py-MS where an attachment to the mass spectrometer allows the sample to be placed in a radio frequency (RF) region continued by an expansion chamber connected to the ion source. The sample is pyrolyzed and the pyrolysate ionized and analyzed in the MS instrument. A schematic diagram of a Curie point Py-MS system is shown in Figure 3.3.2.

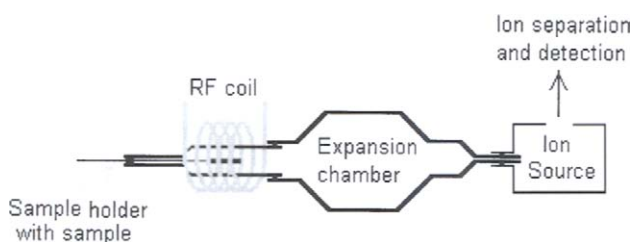


FIGURE 3.3.2. Schematic diagram of a Curie point Py-MS system.

Other techniques utilize lasers for sample evaporation/pyrolysis and excitation such as laser induced desorption (LID) or laser microprobe mass analysis (LAMMA) (see e.g. [1]). Some of the sample introduction procedures in Py-MS enhance the information obtained from Py-MS by the use of time-resolved, temperature-resolved, or modulated molecular beams techniques [10]. In time-resolved procedures, the signal of the MS is recorded in time, and the continuous formation of fragments can be recorded. Temperature-resolved Py-MS allows a separation and ionization of the sample from a platinum/rhodium filament inside the ionization chamber of the mass spectrometer based on a gradual temperature increase [11]. The technique can be used either for polymer or for additives analysis. Attempts to improve selectivity in Py-MS also were done by using a membrane interface between the pyrolyzer and MS [12].

The ionization process that takes place in the ion source of the mass spectrometer can be carried out by standard ionization procedures such as electron impact (EI), by chemical ionization (CI), or by other special techniques (desorption ionization, etc.). In Py-MS, in addition to the decomposition of the sample by heat in the pyrolyzer, the pyrolysate may suffer fragmentations in the MS during the process of ion formation. The ions generated from all the fragments are detected and produce the mass spectrum. The abundance of each mass in the spectrum is the sum of the contributions of all species having charged fragments for that specific mass. This adds significant

complexity to the resulting mass spectrum, which requires special interpretation that is not always straightforward. The result is that the obtained spectrum will not display enough characteristic features to be useful for a diagnostic fingerprint. Some simplification of this picture results from the fact that the fragmentation due to the electron impact on some larger molecules in the MS may generate ions similar to the molecular ions of smaller molecules generated in pyrolysis. Therefore some of the ions seen by the mass spectrometer are generated either by pyrolysis and not fragmented in the mass spectrometer or by the fragmentation of larger molecules due to the ionization in the MS. In order to reduce the complexity of the Py-MS spectrum, various experimental procedures were developed. One procedure to reduce fragmentation in the MS system is the use of low energy EI ionization, where the electron beam has energies of 14–15 eV (instead of 70 eV). These energy values are only a few eV above the ionization potential of most molecules, and the fragmentation at these voltages is lower (but not absent). However, even these energies may produce too much fragmentation, and also small variations in the electron energy are reported to lead to large differences in the mass spectral fingerprints [13].

Other techniques are used for mild ionization of a sample in the mass spectrometer such as field ionization (FI), field desorption (FD), photoionization [14, 15] or using fast atom bombardment (FAB). Field ionization is a very mild ionization technique that generates M^+ or M^- ions from molecules M with low or no fragmentation. This technique consists of placing the compound of interest in an intense electric field. This electric field is created by applying a large electric potential (8–10 kV) between a wire covered with extremely sharp micro-needles (whiskers) and a planar electrode, which also has an exit slit for the ions. The micro-needles can be obtained, for example, by decomposing benzonitrile on a hot tungsten wire. A high charge density is generated at the tip of the micro-needles, and subsequently an intense electrical field (with a gradient of about 10^8 V cm^{-1}) is generated. The ionization takes place when electrons are transferred from the molecules (in positive potential) or to the molecules (in negative potential) via a process called quantum tunneling, generating M^+ or M^- ions respectively. The process takes place with very little vibrational excitation from the electric field, and therefore few or no fragment ions are generated. The ions formed by FI are ejected to the ion separation/detection system of the mass spectrometer. When the sample can be directly deposited on the wire covered with the micro-needles, desorption of the ions formed from the deposited compounds may take place, and the process is called field desorption (FD) [16]. The FD process can be associated with the heating of the wire holding the sample, which is in very low amount ($\sim 10 \text{ ng}$), and pyrolysis of the material can be achieved simultaneously with the desorption process. In addition to the low amount of sample, the high vacuum and the intense electric field cause this process to lack secondary pyrolysis effects. The Py-FD MS generates mainly molecular ions (or $M+1$ ions) from the primary pyrolysis products, and it can be more informative than other Py-MS techniques.

- Other on-line pyrolysis-analytical techniques

Several analytical techniques not associated with GC can be adapted for on-line analysis of pyrolysates. Techniques such as pyrolysis-HPLC (Py-HPLC) and pyrolysis-IR (Py-IR) were reported in literature [17]. In Py-HPLC, for example, the analytical

instrument consists of a typical pyrolyzer connected by a system of valves with an HPLC system. The pyrolysis is performed in the pyrolyzing chamber in an inert gas (such as argon or helium). After the pyrolysis, a solvent flushes the pyrolyzing chamber, dissolving the pyrolysate and carrying it into a retaining chromatographic precolumn. Then, the pyrolysate is back flushed from the precolumn and sent to the analytical column, separated, and further analyzed (see also [1]). The use of an MS system as the detector for the HPLC allows identifications of larger molecules and offers the possibility of gathering information on larger fragments generated during pyrolysis.

A novel, relatively simple method for analytical pyrolysis of polymers is pyrolysis-fractography (Py-F) [18]. In this method, the pyrolysate generated when a polymer is instantaneously pyrolyzed at 600° C is introduced together with the carrier gas into a short length deactivated stainless steel capillary tube. This tube is placed in the oven of a gas chromatograph. The oven temperature is linearly raised, so that the pyrolysate is fractionated based on the distillation temperature, and a fractogram is obtained using a mass spectrometer or a flame ionization detector.

Infrared (IR) techniques are reported in literature to be used in combination with different thermal experiments as a convenient tool of analysis. For example, IR-EGA (infrared evolved gas analysis) was used for obtaining information on different thermal and combustion processes [19]. A simple IR attachment where the sample can be pyrolyzed close to the IR beam is also commercially available (Pyroscan/IR from CDS Analytical). Although the IR detectors are by far not as popular as the MS, pyrolysis-gas chromatography/Fourier transform IR (Py-GC/FTIR) occasionally has been used in polymer analysis. Such applications have been commonly related to the analysis of certain gases such as CO₂, CO, CH₄, NH₃, etc., where the MS analysis is less successful [20, 21].

- Off-line pyrolysis techniques

Off-line pyrolysis can be applied before chromatography as a sample preparation procedure. Although not utilized as frequently as on-line techniques and involving more manual operations, off-line procedures have several advantages. One of these advantages is the possibility to perform additional sample preparation on pyrolysates. For example, specific derivatizations of the pyrolysate can be applied, which may extend the range of compounds analyzed. Silylation of pyrolysate has proven very useful mainly in the analysis of pyrolysates from natural polymers that generate numerous polar fragment molecules [1]. For performing the silylation, the pyrolysate is first collected in a setup as shown in Figure 3.3.3. In this setup, the sample is pyrolyzed in the interface and purged with helium gas such that the effluent is passed through a piece of fused silica capillary. A loop of the capillary is immersed in ice water. After pyrolysis, the capillary is flushed with helium. The capillary is then removed from the ice water bath and the ends inserted into two sealed GC autosampler vials. The first vial contains a solvent and/or a reagent if derivatization is intended (e.g. for silylation the vial contains N,O-bis(trimethylsilyl)-trifluoroacetamide or BSTFA). After the capillary is warmed to room temperature, the material trapped in the tube is dissolved and/or derivatized by repeatedly forcing the liquid through the silica capillary from one vial to

the other using pressure. The vial that finally collects the material can be heated for completing the derivatization.

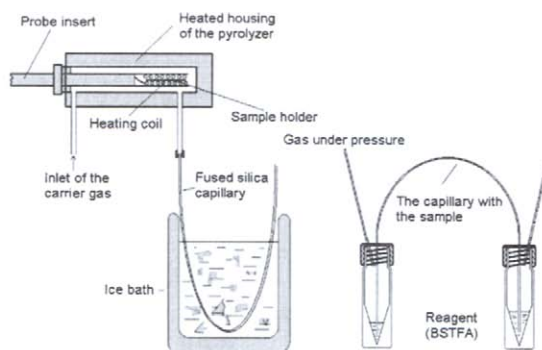


FIGURE 3.3.3. A simple setup for collecting the sample and adding a derivatization agent to the pyrolysate.

Solid phase microextraction (SPME) followed by GC also can be used successfully as an off-line procedure for the analysis of pyrolysates. A simple setup for this procedure is shown in Figure 3.3.4.

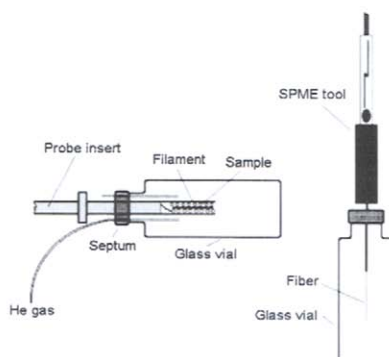


FIGURE 3.3.4. A simple setup for using SPME in the analysis of a pyrolysate.

Typical GC analysis can be performed after the desorption of the SPME fiber in the injection port of a GC instrument [22].

Besides derivatization or selective analysis using SPME, off-line pyrolysis before a chromatographic analysis can be used for various other purposes. One such purpose is the use in the pyrolyzer of larger samples, which would not be appropriate to send directly into a GC instrument. Larger sample must be used in specific applications, for example in the analysis of trace components in pyrolysates. Another application of off-line systems is found when a dedicated GC or GC-MS instrument cannot be afforded only for pyrolysate analysis.

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Information Generated from Analytical Pyrolysis Studies

4.1 QUALITATIVE AND QUANTITATIVE INFORMATION ON POLYMERS

- General aspects

Analytical pyrolysis can be coupled with different analytical techniques for providing information on polymers. Among analytical pyrolysis techniques, Py-GC and Py-GC/MS are probably the most common. The pyrolysis process typically generates a very complex mixture of molecules. For this reason, a chromatographic technique is very important for the separation of pyrolysate components. The fingerprint generated by Py-GC can be used for polymer identification. However, the detection associated with compound identification provided by GC/MS is invaluable in many applications. The exceptional sensitivity and identification capability of mass spectrometric analysis make Py-GC/MS technique the most important analytical pyrolysis technique.

From the composition of pyrolysate, it is usually possible to determine the nature of the polymer or copolymer that generated the pyrolysate. This capability is discussed for many particular cases in Part 2 of this book. However, polymer identification is not the only application used for analytical pyrolysis. Depending on the purpose of the analysis, the minor components in the pyrolysate can be important or not. For example, when the only goal of the analysis is the polymer identification, the main peaks in the pyrogram are the only ones that need to be identified. For other purposes, such as for the search of potentially harmful compounds, a more detailed analysis is required.

Various aspects of analytical pyrolysis and its use in polymer analysis are discussed in a considerable number of publications [1, 2]. These include one journal dedicated solely to pyrolysis, *Journal of Analytical and Applied Pyrolysis*, as well as other journals such as *Polymer Degradation and Stability*, *Macromolecules*, *Journal of Polymer Science*, etc. Also, several books and chapters in monographs cover subjects related to pyrolysis [3–17].

- Peak identification in GC/MS pyrograms

Some polymers have apparently simple pyrograms. The identification of major peaks in these pyrograms is in many cases straightforward and it can be done either using interpretation rules or more frequently by matching the spectrum with standard spectra obtained in EI+ mode with 70 e.V. electron energy found in mass spectral libraries (e.g. NIST 2002, Wiley 7 and their earlier versions). The development of large libraries with standard spectra (over 275,000) and of algorithms for automatic library searches made the use of these tools for spectra interpretation routine. The algorithms for automatic library searches use several criteria for evaluating the quality of a match between the unknown spectrum and a reference spectrum. One well-known algorithm is the Probability Based Matching (PBM) system. This algorithm compares the unknown with all the spectra in the library and has two characteristic features: it weights the mass peaks and performs a reverse search. The reverse search refers to the fact that the algorithm checks whether a peak from the reference spectrum is present in the unknown (and in the appropriate abundance) and not the other way around. In this way,

the reverse search ignores peaks in the unknown that are not present in the reference. As an example, Figures 3.1.7 and 3.1.8 showed the pyrograms of a sample of poly(vinyl ethyl ether) (see Section 3.1). The identification of the major peaks in these pyrograms is given in Tables 3.1.3 and 3.1.4 and was done using mass spectral library searches only.

The mass library searches are in fact elaborate electronic matching routines, which provide at the end a list of possible answers and for each of them a calculated percentage match. The rules for explaining the mass spectrum of a particular compound that were developed to interpret mass spectra without the help of library searches are now more useful for choosing the correct structure from a list of possible compounds identified as candidates by the library search or for obtaining molecular information when the library search does not give a proper answer.

The difficulty of identifying the peaks in a pyrogram increases for the case of low level components. This is due to various interferences in the mass spectra such as background noise, column bleed, and possible misidentifications during the mass library search algorithm. As an example, the pyrogram from Figure 3.1.7 seems to have very few peaks in the time range between 20 min. and 50 min. However, a significant number of small peaks are present in this region. For exemplification, the interval between 20 min. and 50 min. of the chromatogram from Figure 3.1.7, at a different abundance scale about 50 times more sensitive, is shown in Figure 4.1.1.

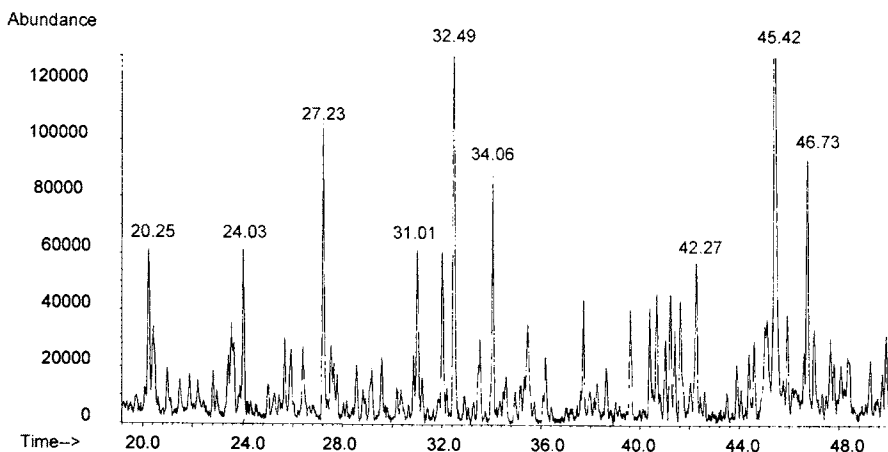


FIGURE 4.1.1. Time window 20 min. to 50 min. from the pyrogram of poly(vinyl ethyl ether) shown in Figure 3.1.7.

A considerable number of peaks can be seen in Figure 4.1.1, each corresponding to a different compound in the pyrolysate. It is not uncommon that not all peaks in a pyrogram are identified. In some cases, the identification of small components is not done by purpose. However, there are many cases when the identification is not possible, either because the spectrum cannot be matched with any spectra from the mass spectral libraries, or because more than one compound is present in a unique peak that was not properly separated by the GC process. In some cases, only tentative assignments can be made. The incomplete analysis of the pyrolysate is not desirable

and plays a role in the variability of the literature reported data on the pyrolysates composition. Some of the pyrolysate components are not identified for a different reason, namely because they are not eluted from the chromatographic column. The use of GC as a separation procedure, as previously indicated, is able to provide results only for a limited range of compounds, which can be eluted from the specific chromatographic column.

As an example, only a few peaks were identifiable based on their mass spectra in the pyrogram window shown in Figure 4.1.1. The results are given in Table 4.1.1.

TABLE 4.1.1. *Compounds tentatively identified in the time window 20.0 min. to 50.0 min. in the pyrogram of poly(vinyl ethyl ether) and shown in Figure 4.1.1.*

Peak	Compound	Ret. time	MW
1	1,1',1''-[methyldynetrtris(oxi)]tris-ethane	20.25	148
2	1-undecene ?	24.03	154
3	1-methoxy-2-propanone ?	27.23	88
4	mixture	31.01	
5	styrene	32.49	104
6	1,3-diethoxy-1-methylbutane	34.06	160
7	5-ethylcyclopent-1-ene carboxaldehyde ?	42.27	124
8	acetic acid	45.42	60
9	mixture	46.73	

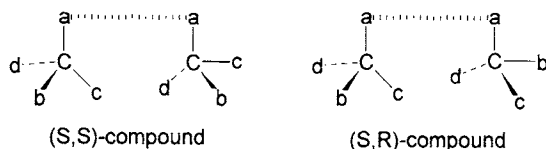
Note: a question mark after the name of a compound indicates tentative identification, and inside the name of a compound indicates tentative position of a substituent, double bond, or conformation.

The tentatively identified peaks shown in Table 4.1.1 can reasonably be considered as formed from the pyrolysis of the polymer. However, some of the peaks could be contaminants in the polymer or from the instrumentation used for the analysis.

Extensive identification of pyrolysate components also may require that the chromatographic separation be done in conditions that allow the elution of compounds with higher molecular weight or with high polarity. This is not always a simple task, since the types of columns that allow the elution of heavier molecules typically do not offer good separation for the early eluting peaks. Also, the mass spectral identification of compounds with higher molecular weight is frequently more difficult than that of lighter compounds since fewer spectra for large molecules are found in the commercial mass spectral libraries. The extension toward higher molecular masses of the range of compounds identified in Py-GC/MS can be done by other procedures, such as derivatization of the pyrolysate (methylation with TMAH for acidic compounds, silylation for alcohols, etc.) or application of specific techniques dedicated for the analysis of a particular class of compounds (see e.g. [17]) and suspected to be present in the pyrolysate. Positive peak identification should be done using authentic compounds with the verification of the retention time in specific chromatographic conditions, as well as the mass spectrum. However, this is very seldom practiced for the identification of the compounds in a pyrolysate.

One additional factor that may add complexity in pyrolysate analysis is the presence of several diastereoisomers for the same compound. Many polymers contain in their backbone asymmetric atoms (usually carbons). A single asymmetric carbon generates two enantiomers, and these are not separated using regular chromatographic columns [17]. The number of stereoisomers of a compound with n chiral centers in the molecule

is equal to 2^n . These stereoisomers can be mirror image one to the other (enantiomers) or may have different steric arrangements being diastereoisomers. Two diastereoisomers are generated from two chiral centers as shown below:



The diastereoisomers can be separated by GC on a nonchiral column because they have different retention times. However, the mass spectra of diastereoisomers are identical. As an example, in Figure 4.1.2 are shown four peaks that have identical mass spectra and are stereoisomers generated from the pyrolysis of poly(vinyl ethyl ether). Four diastereoisomers correspond to eight stereoisomers and consequently to a set of compounds with three chiral centers.

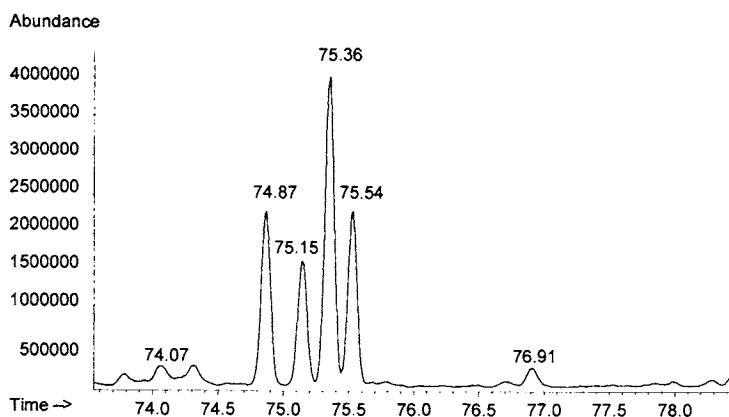


FIGURE 4.1.2. Four peaks with identical mass spectra in the pyrogram of poly(vinyl ethyl ether) (whole pyrogram shown in Figure 3.1.6) corresponding to four diastereoisomers.

One of the four identical mass spectra is shown in Figure 4.1.3.

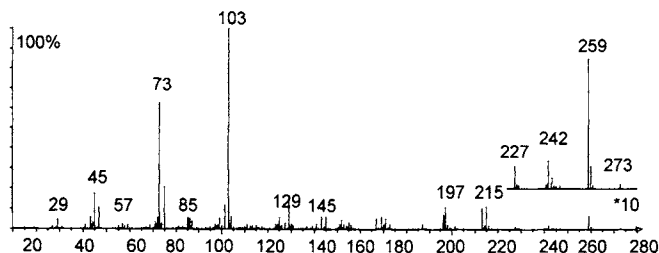
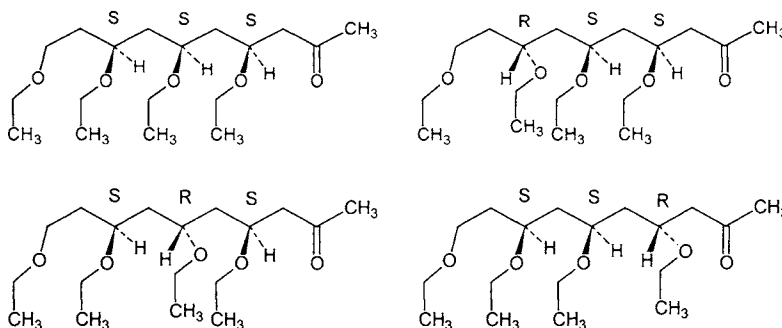


FIGURE 4.1.3. Mass spectrum tentatively assigned to 4,6,8,10-tetraethoxydecane-2-one, identical for all four peaks shown in Figure 4.1.2.

The formulas for the diastereoisomers, tentatively identified as 4,6,8,10-tetraethoxydecane-2-one having three chiral centers in different configurations, are shown below:



The corresponding enantiomers (4R,6R,8R), (4R,6R,8S), (4R,6S,8R), (4S,6R,8R), of the compound shown above are not separated on nonchiral chromatographic columns. The presence of more peaks with the same spectrum can be in some cases a problem in spectra identification. In other cases, such as those with the formation of diastereoisomers, the number of peaks with identical spectra can be a tool for identifying the number of asymmetric centers and of peak identification. The use of a chiral column can be necessary for verifying that certain peaks are generated by diastereoisomers, these peaks being split in two by a chiral separation.

Various ionization techniques applied in association with Py-GC/MS are reported in literature (see e.g. [12]). However, the most common ionization method is electron impact with the detection of positive ions (EI⁺). The chemical ionization (CI) is sometimes used, but CI spectra interpretation is difficult because of the lack of fragmentation and because the reproducibility in CI is affected by the experimental conditions in which the spectra are generated. However, CI spectra provide valuable information regarding the molecular mass of the analyte, and this can be very useful in combination with EI⁺ spectral information.

The characterization of composition of various polymers does not necessarily require a complete analysis of the pyrolysate. The determination of a polymer or copolymer nature can be done with standardized Py-GC/MS techniques that yield reproducible data and use characteristic peaks preidentified for a number of industrially important polymers and copolymers. The data can be used to develop a custom library, which is used to identify the major components in subsequent unknown polymer blends or copolymers [18]. Also, automatic systems for data interpretation from Py-MS experiments have been developed [19, 20].

- Cumulative spectra in Py-GC/MS

An interesting procedure to process Py-GC/MS data is to generate the sum of all spectra of all the peaks in a pyrogram and use it as a fingerprint for the polymer. This technique is somewhat similar to Py-MS, since the separation achieved by the GC is

eliminated. The procedure may appear to have little merit, since the pyrolysate is once separated and then the spectra are merged back. Therefore, particular peak information is lost in this technique. However, the connection of the pyrolyzer directly to a mass spectrometer typically sends too much material in the instrument, unless a very small sample is utilized. Using a GC in front of the MS helps to keep the MS clean. Characteristic cumulative spectra were generated for different polymers, which were collected in a commercially available library [21] searchable for cumulative spectra. Examples of cumulative spectra for the pyrolysates of polyethylene and poly(ethylene glycol) are shown in Figures 4.1.4 and 4.1.5, respectively.

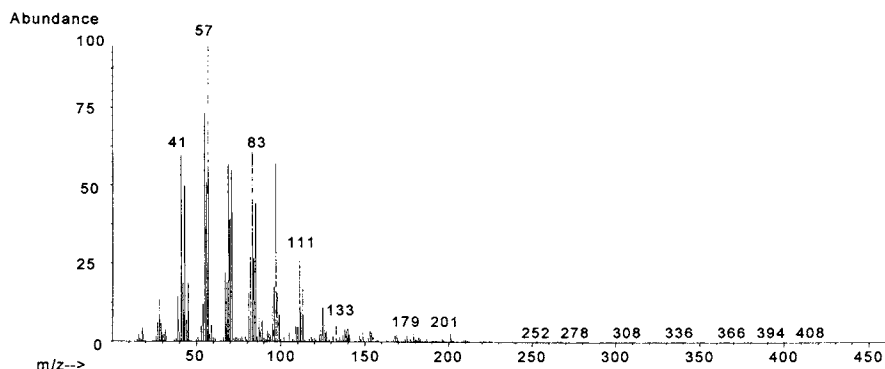


FIGURE 4.1.4. Cumulative spectrum of polyethylene pyrolysate.

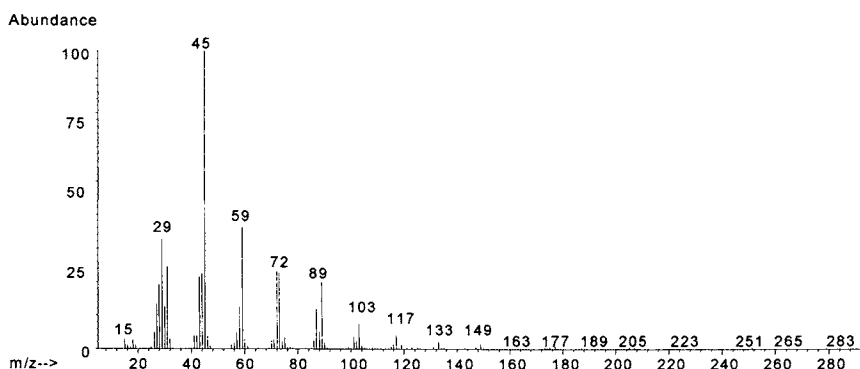


FIGURE 4.1.5. Cumulative spectrum of poly(ethylene glycol) pyrolysate.

These cumulative spectra provide information for polymer identification and can generate some structural hints. The search can be done on the special library or on regular mass spectra libraries (e.g. NIST 2002 or Wiley 7). For the cumulative spectrum of polyethylene pyrolysate, the regular mass spectra library indicates a long chain alkene and for poly(ethylene glycol) indicates bis(2-ethoxyethyl) ether, pointing to the dominant structure in the pyrolysate. However, the use of cumulative spectra is very limited in practice.

- End group analysis using Py-GC or Py-GC/MS

Analytical pyrolysis can be used successfully for the analysis of end groups in polymers. For example, the pyrolysis of poly(methyl methacrylate) obtained from polymerization with benzoyl peroxide as an initiator shows the presence of characteristic aromatic products in the pyrolysate. Peak intensities in the pyrograms of these characteristic compounds allow the evaluation of initiator levels and the understanding of polymerization mechanism [22].

Pyrolysis also has been used for the determination of end group functionalities of macromonomers. For example, polystyrene with methacryloyl end groups can be analyzed using pyrolysis with on-line methylation [23]. For this analysis, the macromonomer in a THF solution was mixed with tetramethylammonium hydroxide (TMAH) and introduced in a two-stage pyrolyzer. The first stage was used to heat the sample at 250° C and decompose the end groups with formation of methyl methacrylate. After the analysis of the methyl methacrylate by GC, the sample was further pyrolyzed at 650° C. The concentration of the end groups was determined by comparing the peak intensities of methyl methacrylate generated from the first stage with those of the polystyrene main chain formed in the second stage of pyrolysis.

Pyrolysis with TMAH derivatization may provide more information regarding the end groups than straight pyrolysis since it may occur at lower temperature and generate fewer polar compounds, which can be analyzed more successfully with chromatography. For example, the structures of some copolymers of polycarbonates were determined with better results using pyrolysis with TMAH than by direct pyrolysis [24].

- Quantitation using Py-GC/MS

Py-GC/MS can be applied for both qualitative and quantitative purposes. One typical use of quantitative analysis using pyrolysis is the determination of the amount of a specific polymer in a given complex matrix, such as a composite material, inorganic matrix, etc. Since solubilization is frequently a very difficult task for these materials, pyrolysis can provide quantitative information based on the level of the polymer marker generated by the thermal decomposition. Calibration is typically necessary in these situations, and similarly to other analytical procedures this can be achieved using a standard addition type procedure (see e.g. [17]) or a calibration with known amounts of polymer in a similar or identical matrix. Another case where the quantitation can be necessary is the determination of the amount of a comonomer in a copolymer sample. Successful quantitation by Py-GC/MS is reported in literature for various copolymers [25–39], etc.

In order to generate reliable quantitative results by Py-GC or Py-GC/MS, an important requirement is the repeatability of the analysis. Any variation of the parameters of the Py-GC/MS analysis may influence the outcome. For this reason, the quantitation using Py-GC/MS is more difficult than that in typical chromatography. The variability is a result of the fact that certain steps in the pyrolytic process may not be perfectly reproducible. Reproducibility is mainly affected when the same sample is analyzed with different types of instruments. However, for the same instrument and the same amount of sample, the reproducibility can be very good. As an example, two pyrograms of 0.4 mg sample of

poly(acrylonitrile-co-methyl acrylate), CAS# 24968-79-4, are given in Figure 4.1.6. The pyrolysis was done at 600° C in He at a heating rate of 20° C/ms with 10 s THT on a CDS 2000 filament pyrolyzer. Between the two pyrograms, 30 other different samples were analyzed. The separation was done on a Carbowax column (60 m, 0.32 mm i.d., 0.32 μ m film thickness) with the GC starting at 40° C with a ramp of 2° C/min. up to 240° C and a final oven time of 20 min. The MS was operated in EI+ mode.

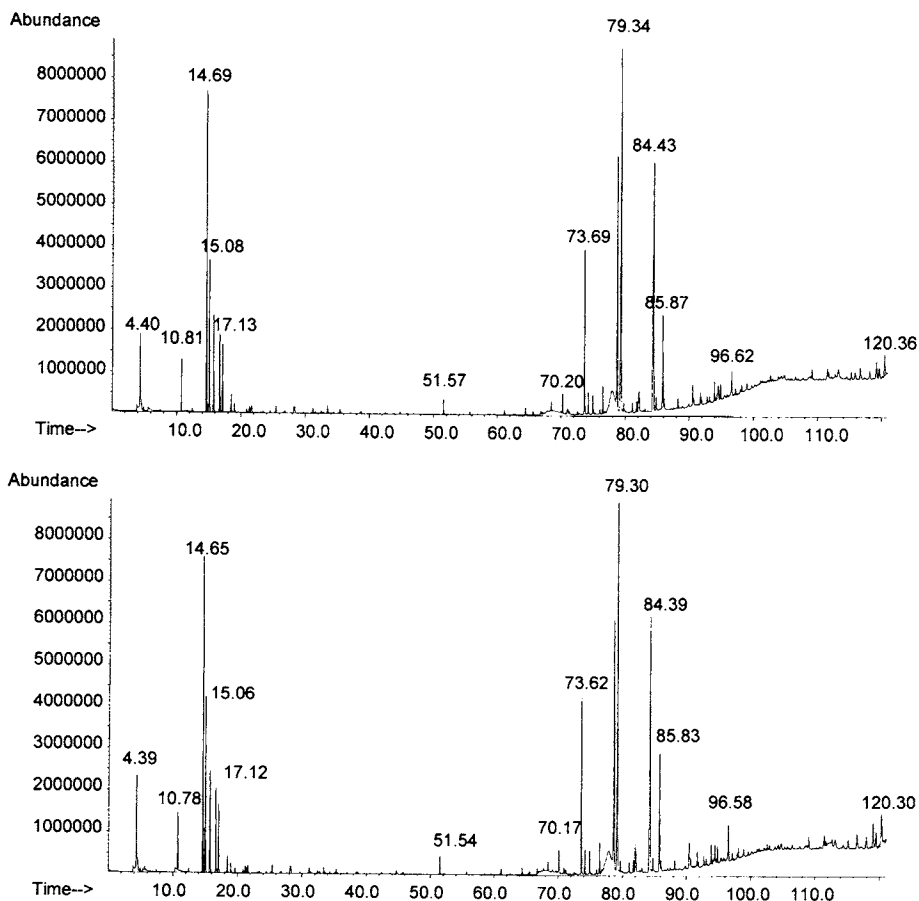


FIGURE 4.1.6. Duplicate pyrograms for samples of poly(acrylonitrile-co-methyl acrylate) analyzed on the same instrument, with 30 different samples analyzed in between.

The similarity between the two pyrograms can be evaluated by inspecting Table 4.1.2, which gives the retention times of 21 selected peaks and the corresponding area ratios.

TABLE 4.1.2. Retention times of 21 selected peaks from the two pyrograms of poly(acrylonitrile-co-methyl acrylate) shown in Figure 4.1.6, and the corresponding area ratios.

Peak	Ret. Time 1	Ret. Time 2	Area ratio
1	4.40	4.39	0.96813
2	10.81	10.78	0.93685
3	14.69	14.65	1.02425
4	15.08	15.06	0.90889
5	15.80	15.75	0.95086
6	16.73	16.66	0.90261
7	17.13	17.12	1.00434
8	51.57	51.54	1.00235
9	70.20	70.17	0.88019
10	73.69	73.62	0.90680
11	74.28	74.21	0.86767
12	75.01	74.93	0.86961
13	76.53	76.45	0.86501
14	78.01	77.92	0.86496
15	78.79	78.73	0.88380
16	79.34	79.30	0.95295
17	84.43	84.39	0.92105
18	85.87	85.83	0.88012
19	93.98	93.90	0.85569
20	96.62	96.58	1.09871
21	120.46	119.03	0.86092

As seen from Table 4.1.2, only minor variations can be seen in the retention time, but although some peaks have about the same area, others may have differences as large as 15%.

The ways to eliminate variability in quantitative work using Py-GC/MS include the use of small sample size and of instruments with the temperature profile well calibrated. The analysis of a standard polymer at specified intervals of time (or number of samples) helps to verify reproducibility, and careful evaluation of the factors that may influence variability followed by their elimination may improve the results. One other procedure to improve reproducibility is the use of an internal standard during pyrolysis. The addition of a standard is not always simple when the sample weight is below 1 mg, and the standard must represent only a small part of the sample. A solution to this problem is to pyrolyze simultaneously with the sample a measured amount of standard diluted in a solid matrix, an example being alumina containing 1% of 1,4-dibromobenzene [40].

Quantitative pyrolysis results can be reported to the initial amount of sample or to specific fractions from the pyrolysate such as the volatiles seen in specific analytical conditions. Reporting the pyrolysis yields to the initial amount of sample can be important in some studies. In this case, either the variation in weight of the initial sample or the quantitation of each component in the pyrolysate (including char) is necessary. For Py-GC/MS, a different procedure can be applied, namely the calibration of the Py-GC or Py-GC/MS instrumentation with an internal standard. Similar to the use of an internal standard (such as alumina containing 1% of 1,4-dibromobenzene) for controlling reproducibility, the addition of several levels of a thermally stable standard in a sequence of pyrolysis experiments can allow the calibration for quantitation purposes. Quantitative results also can be reported, for example, to the total fraction of volatiles.

This is a simpler alternative, but it allows only a relative comparison of the yields of different compounds. The normalization of each peak area in a pyrogram by the sum of all peak areas is a good procedure for identifying which compound is generated at a higher yield compared to the other volatiles. However, it does not necessarily represent the true yield of a volatile compound. Computer programs known as target compound software are available to assist in quantitative analysis, combining the stability of retention times in a given separation with the identification of specific compounds based on several characteristic mass ions. These software packages have the general purpose of quantitation of specific compounds in GC/MS chromatograms and can be applied to Py-GC/MS results. Because of the problems encountered in quantitative Py-GC/MS, its use is typically limited to comparisons and overall characterizations together with qualitative analysis.

- The use of analytical pyrolysis with other polymer analysis techniques

An important aspect of the use of analytical pyrolysis is its capability to provide complementary information to other analytical techniques used for polymer characterization. One such technique is IR analysis of polymers. Although IR spectra can be used as fingerprints for polymer identification, the success of this technique can be questionable when the polymer is not pure or is in a mixture with other compounds. The IR spectra are particularly difficult to use when a polymer is present only at a low level in a particular material and cannot be easily separated. The use of Py-GC/MS allows identification of polymers even in low concentration in specific mixtures because it couples pyrolysis with a chromatographic technique. On the other hand, some polymers generate by pyrolysis a low proportion of easily identifiable molecules, producing mainly char and small uncharacteristic molecules such as HF, H₂O, CO₂, etc. In these cases, IR is the technique of choice. Since for an unknown sample each technique can be misleading, the use of both types of information is always beneficial.

Another technique that can be used successfully together with analytical pyrolysis is thermogravimetric analysis (TGA). TGA provides very useful information regarding the thermal behavior of polymers, such as temperatures of phase change or temperatures of chemical change (decomposition). The analysis of molecules generated during polymer thermal decomposition has been used particularly for gaseous molecules in EGA (evolved gas analysis). Also, some TGA instruments may be coupled with an analytical instrument for the analysis of the volatiles generated during heating, such as an IR spectrophotometer. However, most instruments of this type do not have high enough resolution to be capable of identifying complex mixtures, and the use of analytical pyrolysis at a desired temperature provides significantly more detailed information regarding the decomposition products of a material.

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4.2 STANDARDIZATION OF THE ANALYTICAL PYROLYSIS TECHNIQUES

- General aspects

Analytical pyrolysis has a number of characteristics that can make it a very powerful tool in the study of polymers and composite materials. The technique usually requires little sample and can be set with very low limits of detection for a number of analytes. For Py-GC/MS the identification capability of volatile pyrolysate components is exceptionally good. A range of information can be obtained using this technique, including results for polymer identification, polymer structure, thermal properties of polymers, identification of polymer additives, and for the generation of potentially harmful small molecules from polymer decomposition. In most cases of analysis of a polymer or composite material, the technique does not require any sample preparation, not even solubilization of the sample, which may be a difficult task for the type of materials analyzed. The analysis can be easily automated and does not require expensive instrumentation (beyond the cost of the instrument used for pyrolysate analysis).

One considerable limitation of the application in practice of analytical pyrolysis is caused by the variability in the results and the result interpretation for the same sample in different reported studies. Pyrolysates are typically complex mixtures and the interpretation of results is not always straightforward. The number of constituents in the pyrolysate of a polymer is always high, even for synthetic polymers that decompose by an unzipping reaction and generate a high yield of monomer. The analysis of all components of the pyrolysate is practically unachievable, and setting a limit below which the presence of a specific component is irrelevant is not always a well-defined choice. For this reason the reported results from different studies may have differences. An accurate description of the level of detail reported for a study may eliminate part of the perceived variability in the results for analytical pyrolysis. Within this book there are tables with main pyrolysis products of various polymers, either as reported in literature or obtained as original experiments. The variability in the conditions of pyrolysis as well as the differences in the level of details reported may lead to differences in the description of pyrolysate composition. For a given polymer, these differences are always caused by the use of different conditions of the experiment or by different levels of detail in the description of pyrolysate composition. For this reason, a careful evaluation of the experimental conditions and the understanding of the goal of the study are necessary when evaluating analytical pyrolysis results.

The variability in the temperature of pyrolysis and the true temperature of the sample during pyrolysis frequently has been considered one of the variable parameters. The temperature of the sample during pyrolysis can be standardized between different pyrolyzers using a model compound such as the isoprene/styrene copolymer with the trade name Kraton 1107 [1, 2]. The procedure is based on the dependence of the composition of the pyrolysis products on temperature. Kraton 1107 decomposes generating isoprene, dipentene, styrene, dimethylvinylcyclohexene, and other small molecules. The ratio of isoprene to dipentene was found to be proportional with the pyrolysis temperature between 500° C and 850° C, with a good correlation coefficient (0.964). Several restrictions were imposed on the pyrolysis, such as a heating rate q higher than 2° C/msec and THT longer than 500 msec. The calibration with Kraton 1107 was done by performing the pyrolysis in an inductively heated or a resistively heated filament pyrolyzer and the analysis using a gas chromatographic technique. The

isoprene/dipentene ratio was obtained from the ratio of the chromatographic peak areas of isoprene and dipentene. The study [1] generated the data shown in Table 4.2.1.

TABLE 4.2.1. *The isoprene/dipentene ratio as a function of temperature for the pyrolysis of Kraton 1107 in an inductively heated (Curie point) or a resistively heated filament pyrolyzer.*

Temp. ° C	Isoprene/ dipentene
650	1.76
700	2.52
750	3.21

The dependence of $T^{\circ}\text{C}$ as a function of R = isoprene/dipentene can be given by the expression:

$$T^{\circ} = 527.9 + 68.9 \cdot R \quad (4.2.1)$$

In principle, rel. (4.2.1) allows the calibration of any pyrolyzer for a series of given temperatures with corresponding temperatures acquired by the sample. It is interesting, however, that a study regarding the pyrolysis of Kraton 1107 in a furnace pyrolyzer [3] found linearity between T and R only at temperatures between 450°C and 625°C .

The variability in the results themselves is mainly caused by the large number of parameters that can be adjusted for this technique. Among these parameters are the type of pyrolyzer (filament, Curie point, micro furnace, laser, etc.), and the parameters for the pyrolysis process, such as the (final) equilibrium temperature T_{eq} , the heating rate TRT , the heating time THT , the quantity of sample taken for analysis, etc. When using GC/MS for the analysis of the pyrolysate, the adjustment of the parameters associated with this technique also lead to variability in the final results. Changes in any of these parameters may lead to some problems for the reproducibility (between laboratories), although repeatability of results (performed in the same laboratory and with the same equipment) for experiments performed in identical conditions is very good. This range of potential changes (intentional or unintentional) in the parameters for analytical pyrolysis made the technique less utilized than expected. The reproducibility problem makes, for example, pyrograms obtained in Py-GC experiments less useful as a universal fingerprint for a given polymer. The use of precise standardization for analytical pyrolysis parameters may improve the reproducibility and contribute to the extension of current uses of this valuable technique. On the other hand, since different polymers may require different pyrolysis conditions, the use of identical conditions for all polymers would be an unacceptable limitation. One positive factor in applying analytical pyrolysis for polymer identification is the possibility to analyze the components in pyrolysates using mass spectrometric detection after GC separation. The combination Py-GC/MS is, for this reason, the most common and successful analytical pyrolysis technique.

With a few exceptions, the results for some original experiments described in this book were obtained keeping identical parameters for the experimental conditions of the pyrolysis step as well as for the separation and analysis of the pyrolysate. These particular parameters are described in Table 4.2.2.

TABLE 4.2.2. *Typical parameters for Py-GC/MS experiments described in this book.*

Analytical pyrolysis parameter	Value
Pyrolyzer type	Heated filament*
Experiment type	Flash pyrolysis
Carrier gas	He
Equilibrium temperature T_{eq}	600° C
Temperature rising time TRT	20° C/ms
Total heating time THT	10 s
Sample weight	0.4 mg
Analytical equipment type	On line GC/MS**
Separation column type	Carbowax
Column length	60 m
Column i.d.	0.32 mm
Film thickness	0.32 μ m
Oven initial temperature	40° C
Initial hold time	1 min.
Heating rate	2° C/min.
Final temperature	240° C
Final heating time	20 min.
He flow at 40° C	1.1 mL/min.
Constant He pressure	17.0 psi
Transfer lines temperatures	250° C
MS mass range	10–510 a.u.

* A CDS Pyroprobe 2000 with a CDS AS (autosampler) 2500 was used for pyrolysis.

** A 6890 GC with a 5973 MS system from Agilent was used for pyrolysate analysis

A temperature of 600° C was selected because it is high enough for decomposing most samples and also frequently provides some level of dimers, trimers, etc. that contain more structural information than the monomer alone (see Section 3.1). The separation on a Carbowax column allows better separation of polar compounds compared to most other stationary phases. The limit of 240° C for the heating temperature for this type of chromatographic column is relatively low, and a higher heating temperature would provide a wider window for the temperature range for analyzing the pyrolysate. However, the compounds eluting at higher temperatures have high molecular masses (MW), which are very frequently difficult to identify using the mass spectra. In these conditions, a wider window does not really provide much additional information.

Since pyrolysis of certain polymers may generate relatively large fragments or polar molecules that elute slowly from the chromatographic column, constant care must be taken to avoid carry over problems. In some instances, a blank run is necessary before a new sample to assure that no ghost peaks or carry over compounds are present in the pyrogram. Although this practice uses additional time for running samples, it is not a real problem when the pyrolysis instrument is equipped with an autosampler.

In a few cases the original experiments described in this book were performed at an equilibrium temperature T_{eq} of 850° C. This was done for the case of polymers that are more heat resistant. For these experiments, all the other conditions were maintained the same. When different conditions were used for the experiment (e.g. the use of tetramethylammonium hydroxide, TMAH, for in situ derivatization of pyrolysate, or off line silylation) these modifications as well as any changes in the separation conditions are described with these particular experiments.

One important source of variability in generating similar pyrograms is the sample itself. Variations in the amount of sample may lead to different results for the pyrogram. For this reason, in the experiments described through the Part 2 of this book, the amount of sample was kept as close as possible to 0.4 mg. Most of the samples were obtained from Aldrich (aldrich@sial.com).

References 4.2

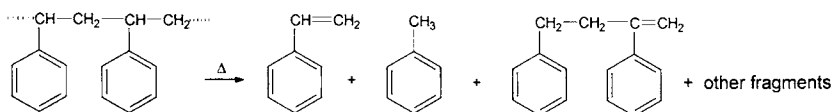
1. E. J. Levy, J. Q. Walker, J. Chromatogr. Sci., 22 (1984) 49.
2. J. Q. Walker, J. Chromatogr. Sci., 15 (1977) 26.
2. P. A. Dawes, M. K. Cumbers, P. A. Hilling, J. High Res. Chrom., 11 (1988) 328.

4.3 STRUCTURAL INFORMATION ON POLYMERS

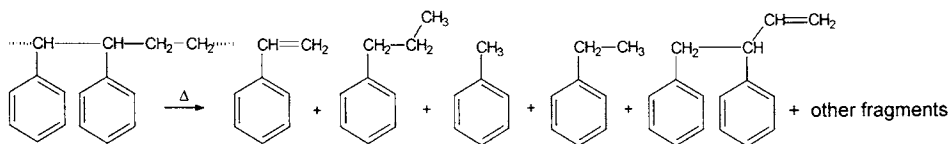
- Study of polymer isomerism

Analytical pyrolysis has been used frequently for providing structural information on polymers (see e.g. [1], including polymer isomerism, which was summarily presented in Section 1.3. For example, pyrolysis studies have been used for the analysis of proportion of head-to-tail (H-T) versus head to head (H-H) isomers in polymers and for the study of stereoregularity [2].

Most vinyl type monomers form during polymerization H-T type polymers. However, a certain proportion of H-H polymer may be formed during radicalic polymerization. An example of differentiation between H-T and H-H polymer using pyrolysis data was reported for polystyrene [3]. Although during pyrolysis the yield of monomer is not different between H-T and H-H polymers, other small molecules may indicate the structural differences, as shown in the schemes below that indicate the main compounds formed in the thermal decomposition process for the H-T polymer:



and for the H-H polymer:

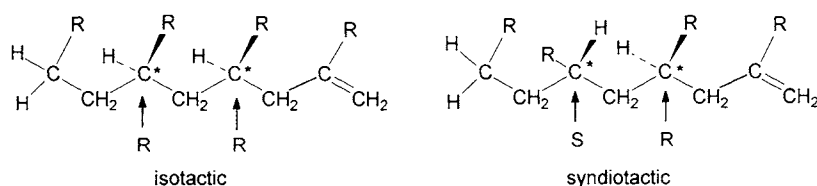


In the pyrolysates from H-H polystyrene, there are noticeable levels of propylbenzene, 1-propenyl-3-benzene, and 3,4-diphenyl-1-butene. These compounds are not present in the pyrolysate of H-T polymer, while 2,4-diphenyl-1-butene is present. The analysis of

the composition of pyrolysates and possible calibration using standard polymers with a known composition can lead to the determination of the proportion of the H-T vs. H-H composition of the polymer.

Study of polymer stereoisomerism

When a polymer contains in the backbone asymmetric atoms (usually carbons), the fragment molecules generated by pyrolysis also will contain asymmetric carbons. The enantiomer molecules are not separated by non-chiral chromatographic columns, but the diastereoisomers, which are in 2^{n-1} number (n is the number of chiral centers), can be separated and generate individual peaks (see also Section 4.1). During pyrolysis, an isotactic polymer will generate predominantly one steric type of fragment while the syndiotactic polymer generates a different steric type. The atactic polymer will generate typically a mixture. For example, for a vinyl polymer the formation of a fragment with two chiral centers can have the (R,R) form or the (R,S) form, which will be separated on a non-chiral chromatographic column. The (S,S) fragment also can be formed but will elute together with the (R,R) fragment, and the (S,R) will elute together with the (R,S) fragment since they are enantiomers. The formation of an (R,R) fragment from an isotactic vinyl polymer and of the (R,S) fragments from a syndiotactic polymer are shown below:



The preservation of the stereospecificity during pyrolysis is not always perfect [4], and some fragments with mixed steric structure are always present.

An example showing the changes in the pyrolysate composition depending on the polymer tacticity can be given for polypropylene. This polymer contains asymmetric carbons and can be synthesized in atactic, isotactic or syndiotactic forms (see Section 5.1). One of the fragments in polypropylene pyrolysate is the hexamer of propylene (MW = 252). This hexamer has four chiral centers and 16 stereoisomers. Since the enantiomers cannot be separated by common chromatographic columns, eight peaks corresponding to the hexamer diastereoisomers are expected in the chromatogram. This is shown in Figure 4.3.1, which gives a time window between 48 min. and 52 min. from the pyrograms of polypropylene. The whole pyrograms are displayed in Figure 5.1.16 (see Section 5.1). The time window from Figure 4.3.1 contains eight labeled peaks corresponding to the propylene hexamers. The dominant stereoisomer of the hexamer generated from the isotactic polypropylene is (R,R,R,R) (and/or (S,S,S,S)). From the syndiotactic polymer, the predominant stereoisomer is (R,S,R,S) (and/or (S,R,S,R)). As seen in Figure 4.3.1, one diastereoisomer is indeed higher in the pyrolysate of the isotactic polymer, and another one is predominant in the pyrolysate of the syndiotactic one.

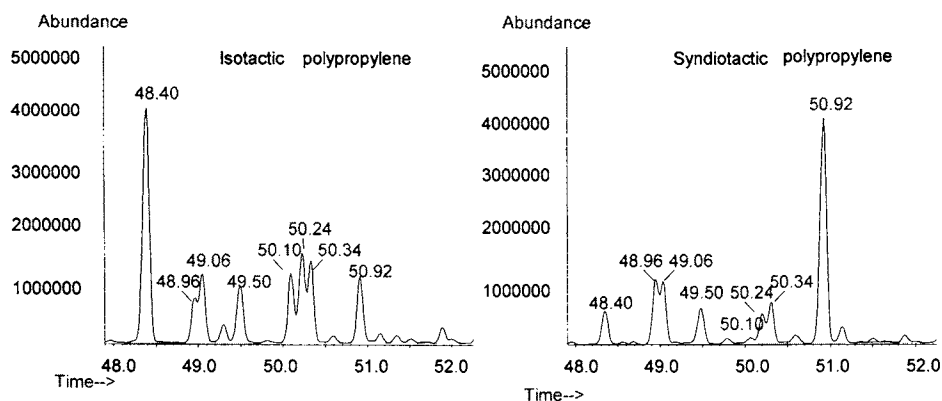


FIGURE 4.3.1. Eight peaks (time labeled) corresponding to the eight diastereoisomers of propylene hexamer. The figure shows a time window from 48 min. to 52 min. taken from the pyrograms of isotactic and syndiotactic polypropylene, which are displayed in Figure 5.1.16.

The hexamer peaks at 48.40 min. and 50.92 min. can be used for the evaluation of stereospecificity of polypropylene after calibration with polymers with known stereoregularity.

The set of diastereoisomers in the time window 48 min. to 52 min. for the propylene hexamers from an amorphous material are shown in Figure 4.3.2. As seen in this figure, the peak intensities for the amorphous PP are somehow similar to those for isotactic PP. However, the intensity for the (R,R,R,R) diastereoisomer (at 48.40 min.) is not as high as that in the isotactic material. The peak for the (R,S,R,S) diastereoisomer (at 50.92 min.) is also present in the pyrogram.

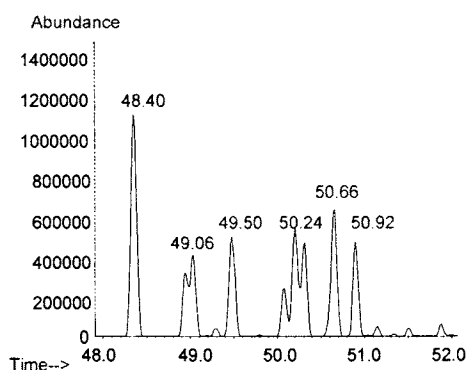


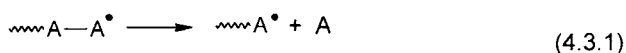
FIGURE 4.3.2. Peaks of the eight diastereoisomers of propylene hexamer obtained from the pyrolysis of amorphous polypropylene. The figure shows the time window between 48 min. and 52 min. from the whole pyrogram, which is displayed in Figure 5.1.21, Section 5.1.

A systematic study of the peak intensity of different diastereoisomers and appropriate calibrations with standards of known composition allows in many cases the estimation of stereospecific type of polymers [5, 6].

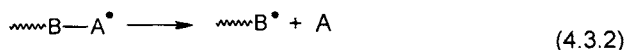
- Study of microstructure of copolymers based on monomer yields

Microstructure of copolymers typically refers to the proportion and the arrangement of the monomer units in the polymeric backbone. In their structure the copolymers may contain the monomeric units arranged randomly, they may alternate regularly, may form large blocks of one type of monomer, or may appear as side chain blocks connected to a polymer main chain (see Section 1.1). This distribution also depends on the relative amounts of each monomer present in the copolymer [7]. Analytical pyrolysis, particularly Py-GC-MS, has been used successfully for the analysis of microstructure of copolymers (see e.g. [8]). Pyrolysis generates small fragments that represent sections of the polymer and can make distinctions between random and block copolymers fairly straightforward.

One parameter typically used for the characterization of distribution of sequences of monomers in a copolymer is the run number (see Section 2.3 and rel. 2.3.33). The run numbers can be determined using the monomer yields during pyrolysis of a copolymer by comparing them with the yields from a homopolymer. The theory is applicable for radicalic mechanisms during the decomposition reactions. Neglecting other effects, it can be seen that a monomer A is generated from a copolymer by two types of reactions:



and



The probabilities of breaking an A-A bond being usually different from the probability of breaking an A-B bond, the yield of monomer is different between the homopolymer and the copolymer (see also rel. 2.3.27 and 2.3.28). A boundary parameter β_A has been introduced to characterize this difference [9] and is defined by the expression:

$$\beta_A = \pi_{AB}/\pi_{AA} \quad (4.3.3)$$

where π_{AB} and π_{AA} are the probabilities given by rel. (2.3.27) and (2.3.28). The relative yield of monomer A from the copolymer pyrolysis Y_A is given by the expression:

$$Y_A = [(\%A-A \text{ bonds}) \pi_{AA} + (\%A-B \text{ bonds}) \pi_{AB}] \quad (4.3.4)$$

Using rel. (2.3.26a) and (2.3.26b) (and replacing R in % with R_i), the expression for the relative yield given by rel. (4.3.4) can be written in the form:

$$Y_A = (F_A - R_i/2) \pi_{AA} + (R_i/2) \pi_{AB} \quad (4.3.5)$$

or using rel. (4.3.3) for β_A , the expression of Y_A becomes:

$$Y_A = \pi_{AA} [F_A - (R_f/2)(1 - \beta_A)] \quad (4.3.6)$$

For a homopolymer $R_f = 0$, and $F_A = 1$. Therefore, $Y_A^0 = \pi_{AA}$, and rel. (4.3.6) becomes:

$$Y_A = Y_A^0 [F_A - (R_f/2)(1 - \beta_A)] \quad (4.3.7)$$

This expression can give the value of β_A :

$$\beta_A = 1 - (F_A - \frac{Y_A}{Y_A^0}) \frac{2}{R_f} = 1 - (F_A - \frac{Y_A}{Y_A^0}) \frac{r_A z^2 + 2z + r_B}{z} \quad (4.3.8)$$

The values of β_A can be obtained for a specific copolymer by measuring experimentally from the pyrolysis results the relative yields Y_A and Y_A^0 , and knowing for the polymer the values F_A , r_A , r_B and z . Such experiments were performed for various copolymers and are reported in literature [9]. From rel. (2.3.22) it can be seen that rel. (4.3.8) can be written in the form:

$$\beta_A = 1 - (F_A - \frac{Y_A}{Y_A^0}) \frac{1}{F_A} (r_A z + 1) \quad (4.3.9)$$

and the value for z can be obtained as a function of F_A by solving the quadratic equation:

$$z^2 (1 - F_A) r_A + z (1 - 2F_A) - F_A r_B = 0 \quad (4.3.10)$$

The resulting expression for β_A will require only the values for F_A , r_A , and r_B .

Rearranging rel. (4.3.7) the expression of R_f can be easily obtained in the form:

$$R_f = \frac{2(F_A - \frac{Y_A}{Y_A^0})}{(1 - \beta_A)} \quad (4.3.11)$$

where F_A , β_A , Y_A and Y_A^0 are obtained from experimental results.

- Study of microstructure of copolymers based on dimer yields

Other procedures to evaluate the copolymer structure are based on the formation during pyrolysis of fragments larger than monomer. Block copolymer will typically produce a pyrogram that appears as the sum of the two pyrograms of the corresponding copolymers (in the case of binary copolymers). Besides the uniform fragments, and depending on the length of the blocks in the copolymer, some larger fragments containing monomers from both types can be present, but these should be in small proportion. For the dimers, the predominant molecules should be A-A or B-B and only a small proportion of A-B type fragments. For the trimers, they should be A-A-A, B-B-B, very little A-A-B or B-B-A, and no A-B-A or B-A-B trimer. At the same time, the random polymers will have a distribution of all possible combinations. The

corresponding random copolymer will produce a much wider distribution of compounds [10] with all the various combinations of monomeric units in the oligomers. The pyrogram will be different from each of the pyrograms for the homopolymers and more complex. This type of behavior has been studied for the copolymers of acrylates [11], for styrene and the polyolefins [2], and for styrene and butyl acrylate [12].

In many copolymers, the block or random structure is only an ideal limit, and a "block character" can be estimated for a binary polymer using the formula [13]:

$$C_{bl} = \frac{N_{bl}}{N_{bl} + N_r} \quad (4.3.12)$$

where N_{bl} is the number of monomer A in blocks, and N_r the number of monomers randomly distributed. Rel. (4.3.12) has been used successfully, for example, for the characterization of poly(ethylene-co-vinylcyclohexene) [13]. In this particular study, the peak areas for the dimeric product (1,3-dicyclohexylpropane) and its unsaturated analogs (S_{bl}) were compared to peak areas corresponding to nonylcyclohexane and its unsaturated analogs (S_r), the areas being proportional to N_{bl} and N_r , respectively. Expressions of the form $N_{bl} = 2 k_1 S_{bl}$ and $N_r = k_2 S_r$ with k_1 and k_2 estimated from polymers with known distribution were used for the calculation of C_{bl} . For poly(ethylene-co-vinylcyclohexene) they were found $k_1 \approx 0.22$ and $k_2 \approx 0.048$.

Copolymers with an *alt* structure are at the other end compared to *block* copolymers. No presence of A-A and B-B dimers should be detected in the pyrolysate, and the only dimer present should be of the A-B type. The trimers should be of the A-B-A or B-A-B type. This makes the pyrogram of an *alt* copolymer different from that of individual homopolymers, except for the presence of smaller molecules than the dimers.

The differences between the copolymers with different microstructures is, however, not always straightforward, and depends on the pyrolysis mechanism. Polymers undergoing side chain reactions may generate a more complex picture for the pyrogram and the quantitative evaluation of block or random character can be more difficult.

A quantitative procedure for the characterization of the distribution of diad sequences in copolymers has been developed [14–19]. In this procedure, the relative yields of dimers Y_{AA} , Y_{AB} and Y_{BB} in the pyrolysate of a copolymer are experimentally determined in order to evaluate the diad concentrations $[P^{AA}]$, $[P^{AB}]$ and $[P^{BB}]$. These concentrations are related to the yields Y_{AA} , Y_{AB} and Y_{BB} by the relations:

$$[P^{AA}] = (1/k_1) Y_{AA}, \quad [P^{AB}] = [P^{BA}] = [1/(2 k_2)] Y_{AB} \quad [P^{BB}] = (1/k_3) Y_{BB} \quad (4.3.13)$$

where $Y_{AA} + Y_{AB} + Y_{BB} = 1$, and k_1 , k_2 , and k_3 are proportionality factors. However, the proportionality factors should be experimentally determined since they are not known. The diads in the pyrolysate are generated from the cleavage of two bonds, one to the right of the diad and the other to the left, such that the value for Y_{AA} can be obtained from an expression of the form:

$$Y_{AA} = [P^{AAAA}] k_{A-AA-A} + 2 [P^{AAAB}] k_{A-AA-B} + [P^{BAAB}] k_{B-AA-B} \quad (4.3.14a)$$

where $[P^{AAAA}]$ is the concentration of the AAAA sequence in the polymer, $[P^{AAAB}]$ is the concentration of the AAAB sequence in the polymer, etc., and where k_{A-AA-A} is the rate constant of formation of the dimer AA from the sequence AAAA, k_{A-AA-B} is the rate constant of formation of the dimer AA from the sequence AAAB, etc. Equivalent relations can be written for Y_{AB} and Y_{BB} as follows:

$$Y_{AB} = [P^{AABA}] k_{A-AB-A} + [P^{AABB}] k_{A-AB-B} + [P^{BABA}] k_{B-AB-A} + [P^{BABB}] k_{B-AB-B} \quad (4.3.14b)$$

$$Y_{BB} = [P^{ABBA}] k_{A-BB-A} + 2 [P^{ABBB}] k_{A-BB-B} + [P^{BBBB}] k_{B-BB-B} \quad (4.3.14c)$$

The concentrations $[P^{AAAA}]$, $[P^{AAAB}]$, $[P^{AABA}]$, etc. can be written in function of $[P^{AA}]$, $[P^{AB}]$, and $[P^{BB}]$ as follows:

$$[P^{AAAA}] = [P^{AA}] (\pi_{AA})^2, \quad [P^{AAAB}] = [P^{AA}] \pi_{AA} \pi_{AB}, \quad [P^{BABA}] = [P^{AA}] (\pi_{AB})^2, \quad (4.3.15.a)$$

$$\begin{aligned} [P^{AABA}] &= [P^{AB}] \pi_{AA} \pi_{AB}, & [P^{AABB}] &= [P^{AB}] \pi_{AA} \pi_{BB}, & [P^{BABA}] &= [P^{AB}] (\pi_{AB})^2, \\ [P^{BABB}] &= [P^{AB}] \pi_{AB} \pi_{BB} \end{aligned} \quad (4.3.15b)$$

$$[P^{ABBA}] = [P^{BB}] (\pi_{AB})^2, \quad [P^{ABBB}] = [P^{BB}] \pi_{AB} \pi_{BB}, \quad [P^{BBBB}] = [P^{BB}] (\pi_{BB})^2 \quad (4.3.15c)$$

where π_{AA} is the probability that an A unit has an A unit on its right (or left), π_{AB} is the probability that an A unit has a B unit on its right, and π_{BB} is the probability that a B unit has a B unit on its right. These probabilities are given by rel. (2.3.27) and (2.3.28) (see Section 2.3). Introducing rel. (4.3.15) in rel. (4.3.14), the following expressions are obtained for the yields:

$$Y_{AA} = [P^{AA}] (\pi_{A-A}^2 k_{A-AA-A} + 2 \pi_{A-A} \pi_{A-B} k_{A-AA-B} + \pi_{A-B}^2 k_{B-AA-B}) \quad (4.3.16a)$$

$$Y_{AB} = [P^{AB}] (\pi_{A-A} \pi_{A-B} k_{A-AB-A} + \pi_{A-A} \pi_{B-B} k_{A-AB-B} + \pi_{A-B}^2 k_{B-AB-A} + \pi_{A-B} \pi_{B-B} k_{B-AB-B}) \quad (4.3.16b)$$

$$Y_{BB} = [P^{BB}] (\pi_{A-B}^2 k_{A-BB-A} + 2 \pi_{A-B} \pi_{B-B} k_{A-BB-B} + \pi_{B-B}^2 k_{B-BB-B}) \quad (4.3.16c)$$

Comparing rel. (4.3.16) with rel. (4.3.13), the expressions for k_1 , k_2 and k_3 can be obtained. The formulas for π_{AA} , π_{BB} , and π_{AB} given by rel. (2.3.27) and (2.3.28) can be introduced in these expressions. The resulting formulas for k_1 , k_2 and k_3 can be written in the form:

$$k_1 = \frac{(r_A z + 1)^2}{Az^2 + Bz + C} \quad (4.3.17a)$$

where $A = r_A^2 k_{A-AA-A}$, $B = 2 r_A k_{A-AA-B}$, $C = k_{B-AA-B}$.

$$k_2 = \frac{0.5(r_A z + 1)(z + r_B)}{Dz^2 + Ez + F} \quad (4.3.17b)$$

where $D = r_A k_{A-AB-A}$, $E = k_{B-AB-A} + r_A r_B k_{A-AB-B}$, $F = r_B k_{B-AB-B}$.

$$k_3 = \frac{(z + r_B)^2}{Gz^2 + Hz + I} \quad (4.3.17c)$$

where $G = k_{A-BB-A}$, $H = 2 r_B k_{A-BB-B}$, $I = r_B^2 k_{B-BB-B}$.

As seen from rel. (4.3.17), the expressions for k_1 , k_2 , k_3 are dependent on the polymer composition, and only the parameters A, B, C, D, E, F, G, H, I are constant, but unknown at this point.

The parameters A, B, C, D, E, F, G, H and I must be determined from experimental data on copolymers with known composition. For this purpose, the pyrolysis yield of dimers Y_{AA} , Y_{AB} and Y_{BB} are measured experimentally for three copolymers with different known compositions. The diad concentrations are obtained for these copolymers from the formulas:

$$[P^{AA}] = F_A \pi_{AA}, \quad [P^{AB}] = F_A \pi_{AB} + F_B \pi_{AB}, \quad [P^{BB}] = F_B \pi_{BB} \quad (4.3.18)$$

where F_A and F_B are the concentrations of the monomer in the polymer and are given by rel. (2.3.22). Using again rel. (2.3.27) and (2.3.28) for π_{AA} , π_{AB} , and π_{BB} , the following formulas are obtained for $[P^{AA}]$, $[P^{AB}]$, and $[P^{BB}]$:

$$[P^{AA}] = \frac{r_A z^2}{r_A z^2 + 2z + r_B} \quad (4.3.19a)$$

$$[P^{AB}] = \frac{2z}{r_A z^2 + 2z + r_B} \quad (4.3.19b)$$

$$[P^{BB}] = \frac{r_B}{r_A z^2 + 2z + r_B} \quad (4.3.19c)$$

and knowing r_A , r_B and z , the diad concentration can be calculated. This will allow the calculation of k_1 , k_2 , k_3 for three known copolymer compositions and further of the constants A, B, C, D, E, F, G, H after solving the corresponding three sets of three equations.

After the formulas for rate constants are known, any diad sequence distribution can be calculated in the copolymer with an unknown composition from the dimer yields. The procedure has been studied for several copolymers including poly(acrylonitrile-co-*m*-chlorostyrene) [17], poly(styrene-co-glycidyl methacrylate) [19], poly(acrylonitrile-co-*p*-chlorostyrene) [17], poly(styrene-co-methacrylate) [20], poly(styrene-co-*p*-chlorostyrene) [18], and for other copolymers [14, 21–29].

- Study of microstructure of copolymers based on trimer yields

The number of triads in a copolymer of AB type can provide information to calculate the number average sequence length $n(A)$ (see rel. 2.3.34). The total number of A monomers can be expressed in triad terms as $N_{AAA} + N_{AAB} + N_{BAA} + N_{BAB}$, where N_{AAA} is the total number of triads containing A found in the polymer microstructure, N_{AAB} is the number of triads containing AAB, etc. The total number of blocks can be expressed

with triad term as $(1/2)N_{AAB+BAA}+N_{BAB}$. Therefore, the expression on $n(A)$ given by rel. (2.3.34) will have the form:

$$n(A) = \frac{N_{AAA} + N_{BAA} + N_{AAB} + N_{BAB}}{(1/2)(N_{BAA} + N_{AAB}) + N_{ABA}} \quad (4.3.20)$$

and a corresponding expression can be obtained for $n(B)$.

The monomer identification in the pyrolysate of a copolymer is usually easily done. Once the monomers have been identified, in order to utilize rel. (4.3.20) to calculate $n(A)$, all the trimer peaks in the pyrogram must be identified. Theoretically, there are eight different trimer peaks in a copolymer system: AAA, AAB, BAA, ABA, BAB, BBA, ABB, and BBB. Their identification is not always simple. However, the AAA and BBB peaks can be identified easily. Since the trimer BAA and AAB have the same molecular mass, they are difficult to distinguish, but the expression for $n(A)$ requires only the sum $N_{BAA} + N_{AAB}$ and they do not need to be differentiated. Pyrolysis of an alternating AB copolymer will allow distinguishing the ABA and BAB, which are the only ones, generated in this case. However, peak identification also can be achieved from retention time comparison or other spectra characteristics.

The next step in the calculation of $n(A)$ is the correlation of trimer peak intensities with the number of specific triads in the polymer. A parameter K can be assigned as a coefficient to express the relationship between the pyrolysis peak area and the triad number. These K values can be obtained by calibrating through copolymers with known composition. A random copolymer of known composition is the best choice in this case since it produces all trimer peaks allowing good calibration. For each trimer type, a simple relation of the type:

$$N_{AAA} = K_{AAA} (\text{Peak area})_{AAA} \quad (4.3.21a)$$

$$N_{BAA} = K_{BAA} (\text{Peak area})_{BAA} \quad (4.3.21b)$$

(where the peak BAA can be arbitrarily assigned between BAA or AAB), etc.

The polymer microstructure based on triad intensities in pyrolysates has been evaluated for poly(styrene-co-butyl acrylate), poly(styrene-co-methyl methacrylate), poly(vinyl chloride-co-vinylidene chloride), poly(styrene-co-maleic anhydride), and for chlorinated polyethylene considered as a copolymer of polyethylene and vinyl chloride [30].

- Other applications of pyrolysis in the study of polymer structure

Other applications of pyrolysis in the study of polymer structure were reported. One such study [31] attempts to use pyrolysis for the selection of composition of polymer blends that have a desired rate of thermal decomposition. The selection of the blending polymer can be based on the assumption that high Φ -factors for monomer pairs in copolymerization would imply that long chain radicals in a degrading blend would preferentially interact, causing mutual termination and reducing the rate of degradation. The Φ -factor is defined for two polymers undergoing polymerization by the expression:

$$\Phi = \frac{kt_{AB}}{2\sqrt{kt_{AA}kt_{BB}}} \quad (4.3.22)$$

where kt are the termination reaction rate constants, the index AB indicating cross termination, while AA and BB indicate like termination.

The system studied by this procedure was poly(styrene) as the host polymer and poly(methyl acrylate) or poly(butyl acrylate) as the blend polymers. The degradation rates were monitored by Py-GC.

The results showed that the Φ -factor proposal alone is too simplistic, and other processes during the radical formation and transfer may play a more important role than termination alone. The rate of degradation of the host poly(styrene) was found to be enhanced and not diminished. However, the degradation rates of the added blend polymer (the acrylates) were reduced by a factor of about eight. Several other studies using the kinetics information on the pyrolysis process were used for the elucidation of the structure of polymeric samples [32–34].

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CHAPTER 5

*Selected Applications of Analytical Pyrolysis in the Study of Synthetic Polymers***5.1 APPLICATIONS FOR THE ANALYSIS OF PLASTICS, FIBERS, ELASTOMERS, COATINGS, AND ADHESIVES****- General aspects**

The analysis of intact polymers, either natural or synthetic, is typically a difficult task. Polymers are not volatile, some have low solubility in most solvents, and some decompose easily during heating. Therefore the application of powerful analytical tools such as gas chromatography/mass spectroscopy (GC/MS) cannot be done directly on polymers. High performance liquid chromatography (HPLC), mainly with the separation based on size exclusion (SEC) / gel permeation (GPC) is frequently applied for the determination of the molecular weight of polymers (see Section 1.6). However, because polymers have a high molecular weight, HPLC coupled with standard MS detection cannot be used for the identification of polymers (see Section 1.6 regarding the use of LC/Fourier transform ion cyclotron resonance mass spectrometry or of MALDI in polymer analysis). On the other hand, pyrolysis of polymers is a simple process that generates mostly small molecules. These can easily be analyzed using GC/MS or other sensitive analytical procedures. Pyrolysis-GC/MS (Py-GC/MS) in particular is a very powerful technique in polymer analysis. From the "fingerprint" of the pyrolysis products, valuable information can be obtained about the initial sample [1–6]. In analytical pyrolysis, instead of adjusting the analytical method for a particular sample, the sample is "adjusted by pyrolysis" for a particularly good analytical technique. Analytical pyrolysis is therefore a special methodology, which allows the use of available powerful analytical methods for the analysis of samples that are not originally amiable to that particular analytical method.

Practical applications of pyrolysis range from the polymer detection and characterization to the microstructure elucidation of specific polymers and to the identification of other compounds present in the polymers (anti-oxidants, plasticizers, etc.). These applications cover analysis of thermoplastics, fibers, paints, adhesives, and elastomers. The analyses can be done for quality control purposes, competitor product evaluation, identification of unknown materials, identifications for forensic purposes, detection of contaminants, etc. Pyrolysis also is used in the study of degradation of polymers during heating. This field is of considerable practical importance, and in parallel with other techniques, analytical pyrolysis is used for polymer thermal characterization [7]. Also, polymer degradation pathways under the influence of heat can be studied using pyrolysis. One more related field is the evaluation of combustibility of samples using pyrolytic techniques, allowing the determination of ignition propensity of different materials. Pyrolysis combustion flow calorimetry has been developed for this purpose [8–10]. In this technique, a small sample is pyrolyzed at controlled temperature in an inert gas stream, the released gasses are mixed with oxygen and combusted, and the heat of combustion is measured. Although the results depend on the sample heating

rate, the process simulates the mechanism of burning and can be correlated with material properties.

- Analysis of various materials

Analytical pyrolysis is used frequently in practice for qualitative identification and for obtaining quantitative or semiquantitative information on samples containing polymers, either synthetic or natural. However, most of this work remains unreported in peer reviewed literature but is rather common in industrial laboratories. Since the objects made from plastic or elastomers are typically insoluble or not easily analyzed by other techniques, analytical pyrolysis is very successful in this type of analysis [11]. The very small amount of material necessary for pyrolysis also allows in many cases performance of the analysis without the destruction of the object to be investigated. Qualitative and quantitative work includes applications for the identification of unknown samples and also for quality control purposes, evaluation of starting materials, evaluation of finished products, reverse engineering and competitor's product analysis, etc. [1]. Among other applications, Py-GC/MS can be used to quantitatively differentiate between natural and synthetic organic materials [12].

Polymers are used frequently in paints and varnishes. These materials are usually filled with opaque materials and are difficult to separate or analyze by other procedures. Pyrolysis can be used to identify the nature of the paint, to measure quantitatively residual monomers, for quality control, and to examine additives [5, 13, 14]. Paints may contain a variety of polymers and copolymers such as vinyl derivatives, polyurethanes, phthalate polyesters, etc. Varnishes may contain various copolymers, siloxanes, etc. and can have a complex composition. This composition can be successfully analyzed using analytical pyrolysis. For example, the composition of a coating material consisting of the terpolymer poly(2-hydroxyethyl methacrylate-co-butyl acrylate-co-ethyl methacrylate) crosslinked with butoxy melamine resin has been analyzed with excellent results based on various monomer ratios resulting from pyrolysis at 590° C [15].

A very useful technique applied for the analysis of paints is on-line pyrolysis associated with thermally assisted hydrolysis and methylation followed by GC/MS analysis (THM-GC/MS) [16]. Compounds such as tetramethylammonium hydroxide (TMAH) are used frequently as reagent (see Section 2.1). This reagent is particularly useful in the analysis of acrylic paints, since acrylic acid and methacrylic acid as well as other acids in the pyrolysate can react easily with the reagent, generating methyl esters that are diagnostic in the analysis of paint [17]. Polymers also are used as carrier material for inks. In addition to the solvent and the pigment used in inks, the analysis of the ink carrier can be done using analytical pyrolysis. Resins used in coating colors also have been analyzed with analytical pyrolysis [18].

Adhesives represent another large group of materials made from synthetic polymers that can be successfully analyzed by pyrolytic techniques such as Py-GC/MS. Adhesives may include styrene, styrene/isoprene blends, vinyl alcohol, vinyl acetate, epoxy resins, acrylates, cyanoacrylates (superglue), ethylene/vinylacetate (hot-melt), polyurethanes, etc. [19].

An important field of applications for analytical pyrolysis is the analysis of synthetic and natural rubber and of rubber blends. Some applications of analytical pyrolysis on this subject are discussed in Section 7.1 and 7.2. Many other applications are reported in literature, including some discussing the formation of various pyrolysis products in the processing of used tires [20, 21].

Among the materials analyzed using analytical pyrolysis are different types of oils and lubricants. Many oils and lubricants used in practice are synthetic oligopolymers or solutions containing polymers for the control of the oil properties. Even when the oil contains a considerable amount of hydrocarbons, the presence of polymeric ingredients can be detected and measured quantitatively using pyrolysis techniques [22, 23].

Other polymeric materials such as those used in cosmetic products, medical drugs, detergents, etc. also can be analyzed using pyrolytic techniques [24]. Several pyrolysis studies were performed to monitor processes involving a polymer. As an example, the enzymatic degradation behavior of poly(ϵ -caprolactone) (PCL) with an α -benzyloxy terminal during an enzymatic degradation test using cholesterol esterase was evaluated by pyrolysis-gas chromatography (Py-GC) in the presence of tetramethylammonium hydroxide (TMAH). On the pyrograms of PCL samples, dimethyl derivative of ϵ -caprolactone and some related products originating from ϵ -caprolactone units were observed together with those from benzyloxy terminal units such as benzyl methyl ether. The relative content of the benzyloxy terminal unit in the residual PCL sample after the degradation test was estimated from the relative intensities of the specific fragment molecules. The level of benzyloxy terminal unit considerably decreased especially in the initial stage of the degradation test. The results suggested that the enzymatic degradation of the PCL might proceed mainly in the *exo*-cleavage mode from α -benzyloxy terminal side [25].

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5.2 APPLICATION OF ANALYTICAL PYROLYSIS FOR THE UNDERSTANDING OF LARGE-SCALE POLYMER PYROLYSIS

- General aspects

Various studies involving small-scale pyrolysis are performed for modeling large-scale pyrolysis. Among the most frequent materials that were studied for both waste reduction and material recovery are used tires. Thermal decomposition of tire material leads to the formation of a complex mixture of C_6 – C_{24} organic compounds, with high content of aromatics (53.4–74.8%), some nitrogenated compounds (2.47–3.5%) and some oxygenated compounds (2.29–4.85%). This mixture has a gross calorific value of 42 MJ kg^{-1} , even higher than that specified for commercial heating oils, but also it has a high sulfur content (1–1.4%), which is of environmental concern. Significant quantities of valuable light hydrocarbons such as benzene, toluene, xylene, limonene, etc. also are obtained. The concentrations of these compounds increase with temperature up to 500°C and then decrease. An important proportion of polycyclic aromatics is also formed including naphthalenes, phenanthrenes, fluorenes, diphenyls, etc. The concentration of total aromatics increases significantly with the heating temperature [1]. A number of other pyrolysis studies are dedicated to the thermal decomposition of used tires [2–5]. Specific aspects of the use of tire waste also have been reported, such as the use of pyrolytic char from pyrolysis of the used tires [6].

Other materials in waste that is thermally processed also were studied by pyrolytic techniques, typically with the purpose of regenerating the monomers or of obtaining other useful small molecules. For example, pyrolytic studies were performed for the evaluation of the possibilities for re-utilization of nylon carpet waste [7], the recycling of thermoset polymeric composites [8], the recovery of methyl methacrylate from poly(methyl methacrylate) waste [9], as well as for other raw material recovery from pyrolysis of plastic waste [10]. The results of incineration of various other types of waste also were studied at model scale [11, 12]. These studies were applied to specific waste materials associated with the manufacturing process or to municipal solid waste [13–15].

The pyrolysis process for waste recycling is frequently done at larger scale than analytical pyrolysis. However, analytical pyrolysis studies are performed independently for the understanding and the optimization of such processes [10, 16–19]. Also, model mixtures can be used in parallel with real samples. For example, the comparison of thermal degradation products from real municipal waste plastic and model mixed plastics can help understand the compounds generated in waste incinerators. In one such study [20], analytical pyrolysis of real municipal plastic waste obtained from Sapporo, Japan and model mixed plastics was carried out at 430°C in atmospheric pressure by batch operation. The chlorinated hydrocarbons found in degradation liquid products of poly(ethylene)/poly(propylene)/poly(styrene)/poly(vinyl chloride) and other polymeric mixtures were monitored. It was determined that the presence of poly(ethylene terephthalate), in addition to chlorinated plastics in the waste, facilitates

the formation of more organic chlorine content in liquid products and drastically decreases the formation of inorganic chlorine content. Similar studies were carried out on other plastic materials including polymers with brominated flame retardants [21] and fiber-reinforced polymeric waste [22]. Some studies also were performed on the thermal decomposition of mixtures of synthetic polymers and natural polymers such as wood or paper [23].

Considerable effort has been invested in the study of pyrolysis using various catalysts or specific conditions during thermal decomposition in order to generate compounds that are different from those obtained by simple thermal decomposition and that have better usability [24–31]. As an example, in a recent study scrap tires were pyrolyzed in a fixed bed reactor, and the evolved pyrolysis gases were passed through a secondary catalytic reactor with the purpose of maximizing the concentration of single ring aromatic compounds. These compounds have high commercial value. Three types of zeolite catalyst were examined of different surface acidity and pore size. The results showed that the influence of the catalyst was to reduce the yield of oil with an increase in the gas yield. A considerable increase in the concentration of certain single ring aromatic compounds was demonstrated in the oils after catalysis. The yields were related to the different properties of the three catalysts such as pore size and the silica/alumina ratio, which influenced the number of catalytically active sites on the catalyst surface [32]. Another example is the study of electronic scrap, which may contain phthalic polyesters filled with ceramic fibers flame-retarded with brominated polystyrene, and printed circuit boards made of epoxy resins on woven glass fiber support flame-retarded with brominated epoxy resins. These materials were pyrolyzed in the presence of sodium hydroxide and basic zeolites. The pyrolysis of the material containing brominated polystyrene generated considerably less dibromo- and tribromostyrenes. The brominated epoxy resins pyrolyzed with sodium hydroxide enhanced bromomethane evolution and depressed brominated phenol formation [33].

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5.3 THE USE OF ANALYTICAL PYROLYSIS IN ENVIRONMENTAL STUDIES AND HEALTH ISSUES

- General aspects

Analytical pyrolysis also has been used for obtaining information on the resulting chemicals during the burning of different materials [1]. It should be noted that burning consists of several processes including combustion (which is the chemical reaction with oxygen and leads most organic compounds to form CO_2 , CO , H_2O , N_2 , and NO_x), volatilization and entrainment of some components, as well as pyrolysis. Incomplete burning (smoldering) and the pyrolysis around the burning area generate pyrolysates that can have complex compositions. Their analysis can be important in connection with health issues and environmental problems [2–7].

Polyurethanes, for example, are widely used in the manufacture of commercial products such as foams and paints. During thermal degradation, such polymeric systems can generate a wide range of combustion products, including isocyanates. These may represent hazards for workers potentially exposed to combustion products, for example in car repair shops. It is therefore important to understand the principal mechanisms involved in thermal degradation of these materials, with particular attention to the isocyanates formation [8]. Py-GC/MS has been used for the investigation of polyurethanes. For example, analysis of diphenylmethanediisocyanate polyurethane foam can be done using pyrolysis temperature of 400°C . In a recent study [9], metastable atom bombardment (MAB) ionization was used to ionize the analytes. This allows modulation of the ionization energy by simply changing the ionization gas. Only molecular ions are observed with MAB using N_2 as the ionization gas. Temperature gradients can be used to separate the products generated during the thermal

degradation of a 1,6-hexamethylenediisocyanate polyurethane paint. Changing the MAB ionization gas allows elucidation of the structure of the pyrolysis products by controlling the extent of their fragmentation. During these experiments, the levels of various noxious gases including isocyanic acid, methyleneisocyanate, ethyleneisocyanate, propylisocyanate and butylisocyanate were measured. Other similar studies were performed on polyamides [10], polyamides in the presence of poly(vinyl chloride) [11], etc.

A considerable number of reports regarding the formation of compounds that may represent a health hazard are related to the formation of polycyclic aromatic hydrocarbons (PAHs) during industrial pyrolysis processes (recycling of waste, incineration, etc.). This interest is particularly geared toward the study of polyolefins pyrolysis and synthetic and natural rubber pyrolysis. The formation of PAHs during polyethylene pyrolysis has been reported frequently in literature [6, 12] and is further discussed in Section 6.1. The formation of PAHs during tire pyrolysis is also of considerable concern. The concentrations of some components in the oils generated from the pyrolysis of used tires as a function of temperature are indicated in Table 5.3.1 [13].

TABLE 5.3.1. *The concentrations (in ppm) of light aromatic hydrocarbons in tire pyrolysis oils as a function of temperature [13].*

Compound	Temperature					
	450° C	475° C	500° C	525° C	560° C	600° C
benzene	<5	55	770	2950	70	605
toluene	2250	3200	6095	17740	7770	5070
ethylbenzene	250	235	120	405	370	190
1,2-dimethylbenzene	2780	3190	3345	5710	5875	3530
1,4-dimethylbenzene	2750	2665	3620	6880	8350	3120
styrene	1205	1705	1950	3545	3635	1915
1,3-dimethylbenzene	920	1020	1325	2450	2570	1040
trimethylbenzene	840	825	1255	085	1285	820
trimethylbenzene	1050	1265	1670	1240	1530	1200
trimethylbenzene	1550	1350	2370	2320	3210	1450
methylstyrene	730	570	1090	1145	1590	715
trimethylbenzene	1075	1070	1325	1295	1395	1095
4-methylstyrene	730	570	1090	1145	1590	715
trimethylbenzene	370	440	490	675	320	330
methylstyrene	6020	6025	7630	8865	9030	6950
limonene	31320	30330	29010	28965	24590	25130
indene	2190	2630	3175	3090	3105	1560
naphthalene	465	420	725	1115	665	1630
2-methylnaphthalene	650	570	730	770	1005	2365
1-methylnaphthalene	460	490	625	645	895	1570
biphenyl	1030	1040	1630	885	1320	3000
1-ethylnaphthalene	430	510	690	830	745	1335
2,6-dimethylnaphthalene	565	565	855	755	995	1990
1,7-dimethylnaphthalene	550	440	365	1020	700	560
1,6-dimethylnaphthalene	275	600	595	715	485	1085
1,5-dimethylnaphthalene	190	305	375	1440	635	880
1,2-dimethylnaphthalene	770	405	600	450	460	1385
acenaphthene	560	580	635	700	620	1070
trimethylnaphthalene	765	470	670	1050	605	825
trimethylnaphthalene	665	515	425	330	830	1570
trimethylnaphthalene	155	175	220	695	430	710

TABLE 5.3.1 (continued). *The concentrations (in ppm) of light aromatic hydrocarbons in tire pyrolysis oils as a function of temperature [13].*

Compound	Temperature					
	280	210	325	290	295	605
fluorene	280	210	325	290	295	605
methylfluorene	65	180	135	90	240	585
2-methylfluorene	115	245	220	175	335	745
1-methylfluorene	260	340	370	310	450	555
?-methylfluorene	135	200	170	320	195	280
phenanthrene	95	230	200	125	195	315
anthracene	85	160	125	135	225	295
dimethylfluorene	215	425	425	165	320	465
2-methylphenanthrene	595	495	315	470	815	1240
2-methylantracene	455	640	500	1010	720	1140
4-methylphenanthrene	355	200	140	275	605	730
1-methylphenanthrene	505	890	470	585	600	555
dimethylphenanthrene	745	1200	520	650	760	1290
2,7-dimethylphenanthrene	1255	1300	1740	525	1060	1075
dimethylphenanthrene	105	120	455	350	1260	540
fluoranthene	120	325	325	355	790	1100
dimethylphenanthrene	730	>5	490	445	1490	1210
dimethylphenanthrene	440	385	305	615	5195	370
pyrene	530	105	120	425	225	115
trimethylphenanthrene	530	400	600	470	520	940
trimethylphenanthrene	30	35	65	35	30	150
chrysene	30	15	35	>5	30	60

As seen from Table 5.3.1, the level of PAHs in tire pyrolysate is relatively high. The use of catalysts has been evaluated for decreasing these levels [14].

Health issues can be related not only to the pyrolysis products of the polymer itself, but also may be related to the compounds that come from the polymer additives. For example, in a study of pyrolysis of high impact polystyrene with decabromodiphenyl ether/antimony oxide added as a flame retardant, it has been shown that toxic polybrominated dibenzofuranes are generated during thermal decomposition in the range of 350–400° C [15].

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5.4 APPLICATIONS OF ANALYTICAL PYROLYSIS TO THE ANALYSIS OF FORENSIC EVIDENCE, CULTURAL MATERIALS, ETC.

- General aspects

Specific characteristics of analytical pyrolysis make this technique extremely valuable in the analysis of forensic evidence [1]. The variety of samples used as forensic evidence may include fibers, paints, inks, small pieces of objects, etc. Analytical pyrolysis, requiring very small samples and having excellent capability in identification of unknown materials is perfectly suited for these analyses. Among other forensic applications of analytical pyrolysis, one is related to the characterization and identification of pyrolysis products that may interfere with the analysis of fire debris. The main purpose of the analysis of fire debris is the isolation and analysis of the target compounds that characterize ignitable liquid residues (ILR). Complex organic mixtures such as automobile gasoline, diesel fuel and other volatile mixtures that could be used to accelerate an intentionally set fire are routinely identified in forensic laboratories. The presence of these target compounds suggests the presence of ILR originating from these mixtures, and this information could aid a fire investigator in determining the cause of the fire, including whether or not arson may have been involved. Analytical pyrolysis can be applied for the characterization of the products resulting from controlled burns of materials commonly found in homes and businesses in order to determine their chemical composition. A list of compounds found from the pyrolysis (and combustion) of different substrate types is further compared with the target compound list for the identification of ILR [2].

Throughout the 20th century a number of binding media, including synthetic resins, have been employed in paints. Pyrolysis GC/MS in the presence of reagents such as tetramethylammonium hydroxide (TMAH), leading to thermally assisted hydrolysis and methylation-gas chromatography-mass spectrometry (THM-GC/MS), can be used for the identification of a wide variety of binding media employed in 20th century art. In a recent study [3] THM-GC/MS was successfully used for the study of binding media in samples from paintings by Jackson Pollock and by Fiona Banner. In another study, artists' acrylic emulsion paints were analyzed by direct temperature resolved mass spectrometry and laser desorption ionization mass spectrometry [4]. The paints were analyzed by thermal separation and ionization of organic pigments and polymeric fractions from a platinum/rhodium filament inside the ionization chamber of the mass spectrometer. Most organic pigments in modern paints are desorbed at lower temperatures. Ethyl acrylate/methylmethacrylate or butyl acrylate/methylmethacrylate copolymers used in acrylic emulsion paints produce mono and oligomeric subunits released from the copolymers at high temperature by pyrolysis. Characteristic low voltage electron ionization and ammonia chemical ionization (CI) mass spectra of these copolymers facilitate their identification. The azo pigments also can be analyzed using direct temperature resolved mass spectrometry. Laser desorption ionization mass spectrometry (LDIMS) using a nitrogen laser (337 nm) can be applied for the analysis of other organic pigments.

References 5.4

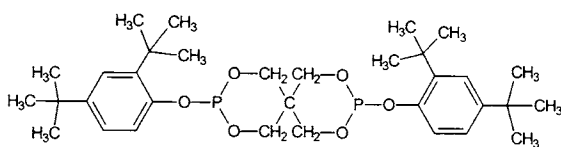
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5.5 ANALYSIS OF SMALL MOLECULES IN SYNTHETIC POLYMERS USING ANALYTICAL PYROLYSIS

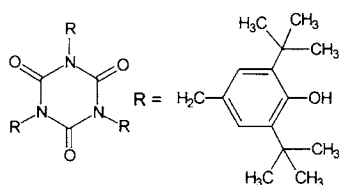
- General aspects

The additives in polymers are analyzed using many different procedures, and many of these procedures require examination of extracts, dissolution of the polymer, chemical modifications of the sample using for example hydrolysis, etc. The analysis of additives especially when they are insoluble can be done successfully using pyrolytic techniques. A number of reports are dedicated to the analysis of additives using analytical pyrolysis [1–3]. However, a considerable volume of work on the analysis of additives using pyrolysis consists of routine procedures in industrial laboratories, and it is not reported in peer-reviewed journals. Also, since most additives are small molecules, a detailed description of pyrolysis studies on additives is not included in this book.

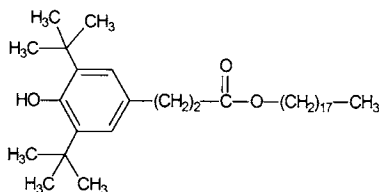
Many procedures for the analysis of additives are based on standard Py-GC/MS instrumentation. As an example, the identification of different flame retardants including tetrabromobisphenol A, octabromobisphenyl, octabromodiphenyl oxide, and decabromodiphenyl oxide in different polymers including poly(acrylonitrile-co-butadiene-co-styrene), high impact polystyrene, and recycled polymer scrap has been reported as performed on a Curie point pyrolyzer coupled with a GC/MS system [4, 5]. Other analyses were done on butylated hydroxytoluene (BHT) in polychloroprene [6], sodium dodecylbenzene sulfonate in poly(ethylene glycol) [7], Tinuvin 144 CAS# 63843-98-0 (light stabilizer), Tinuvin 770 CAS# 52829-07-9 (light stabilizer), Hostavin N20, Tinuvin 622, and Chemiasorb 944 in polyethylene and polypropylene [8], [9], distearylthiodipropionate (DSTDP) in polypropylene [10], 2,6-di-*tert*-butyl-p-cresol in butadiene/styrene copolymer [11], etc. Other procedures apply Py-MS and do not use a GC separation, concentrating the analysis effort on the utilization of the MS instrument for increasing selectivity. In a study of additives used as antioxidants and light stabilizers in polypropylene, the analysis was successfully performed using Py-MS with different ionization procedures including EI+, CI, field ionization (FI), and field desorption (FD) [12]. By using Py-MS/MS and Py-FI/MS it was possible to analyze Irganox 1076 CAS# 2082-79-3 (antioxidant), Tinuvin 144, Ultrinox 626 CAS# 26741-53-7 (antioxidant), Irganox 3114 CAS# 2767662-6 (antioxidant), Tinuvin 770, and GoodRite (UV absorber/antioxidant). The formulas of some additives analyzed using pyrolytic techniques are shown below:



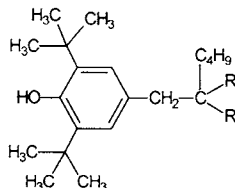
bis(2,4-di-*tert*-butyl)pentaeerythritol diphosphite
(Ultrinox 626)



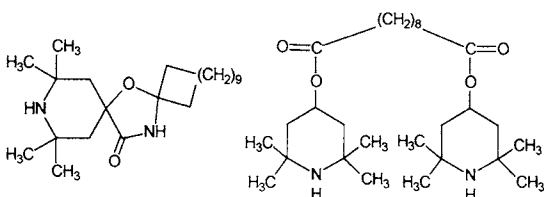
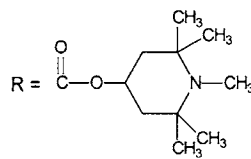
1,3,5-tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)-
isocyanurate (Irganox 3114)



octadecyl-3,5-di-*tert*-butyl-4-hydroxy-
hydrocinnamate (Irganox 1076)

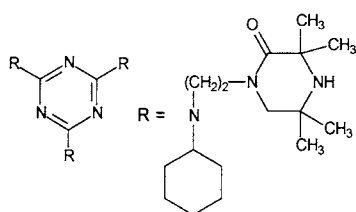


2-*tert*-butyl-2(4-hydroxy-3,5-di-*tert*-butylbenzyl)[bis(methyl-
2,2,6,6-tetramethyl-4-piperidinyl)]dipropionate (Tinuvin 144)



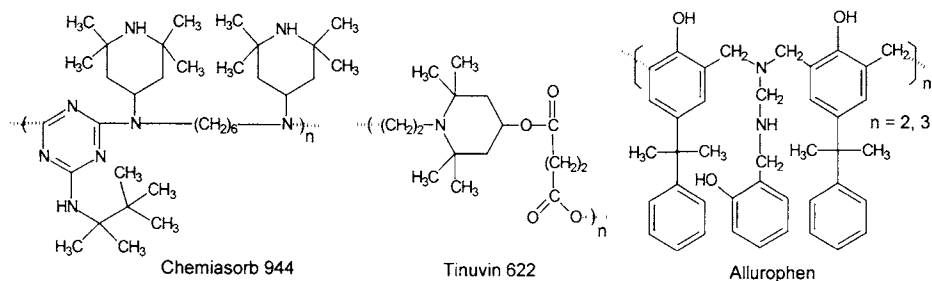
Hostavin N20

bis(2,2,6,6-tetramethyl-4-piperidinyl)
sebacate (Tinuvin 770)

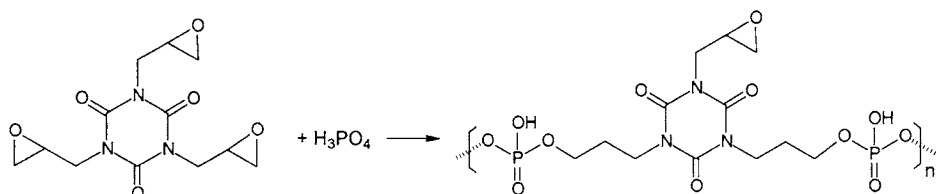


2,4,6-tris[1-[2-(cyclohexylimino)ethyl]-3,3,5,5-
tetra-methylpiperazin-2-one]-1,3,5-triazine
(GoodRite 3150)

Some additives are themselves polymeric (or oligomeric). For example, among the compounds used as light stabilizers in polypropylene are Tinuvin 622, which is poly (1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxy-piperindinyl succinate) CAS# 65447-77-0, and Chemiasorb 944, which is poly-[(1,1,3,3-tetramethylbutyl)amino]-1,3,5-triazine-2,4-diyl-[(2,2,6,6-tetramethylpiperidinyl)imino]-hexane-1, 6-diyl-[(2,2,6,6-tetramethylpiperidinyl)imino] CAS# 71878-19-8. Their analysis has been done using FD/MS, Py-CI/MS and Py-CI/MS/MS and was based on the identification of the monomers and oligomers generated from the thermal decomposition of these compounds [12]. Another example of oligomeric additive is the antioxidant Allurophen used mainly in rubber. The thermal decomposition of this material has been studied and reported in literature [13]. The structures of Chemiasorb 944, Tinuvin 622, and Allurophen are shown below:



Among the additives with polymeric structure are the condensates of triglycidyl isocyanurate with orthophosphoric and polyphosphoric acids, which are used as flame retardant additives, for example, in polypropylene. These additives are obtained from reactions as shown below:



The study of these materials using pyrolytic techniques allows understanding of the formation of high temperature resistant residue and the flame retardancy mechanism [14]. Some other pyrolytic methods for additives analysis utilize specially constructed equipment. For example, one method reported in literature [15] is based on a double-shot pyrolyzer coupled to a GC/MS instrument. The volatiles are generated in the first step pyrolysis, and further analysis is performed after pyrolysis in the second stage at higher temperature. The identification of the volatile additives can be achieved directly on the basis of their mass spectra, while that of nonvolatile materials is based on the identification of fragments generated by pyrolysis [15]. The results were exemplified only for the analysis of acrylonitrile/butadiene/styrene terpolymer (recycled ABS and virgin ABS), but various other materials can be analyzed using this technique.

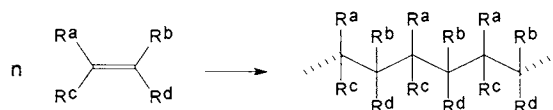
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CHAPTER 6

*Polymers with Saturated Carbon Chain Backbone***6.1 POLYOLEFINS****- General aspects**

Polyolefins are hydrocarbon polymers with the backbone formed from a chain of aliphatic carbon atoms. These polymers are typically obtained in a reaction shown schematically as follows:



where R^a , R^b , R^c , R^d , are hydrogens, alkyls, and/or cycloalkyl radicals. This class includes polymers such as polyethylene, polypropylene, polyisobutene, etc. Some of the polymers from this class are vinyl polyhydrocarbons because they are obtained from the polymerization of a vinyl derivative of the form $\text{CH}_2=\text{CHR}$. However, only a few polyolefins use the name vinyl, one example being polyvinylcyclohexane. The name vinyl is more common for other polymers where R is not of hydrocarbon type. Most polyolefins have a backbone consisting of a linear chain of carbon atoms. However, chain branching can be present and may lead to the modification of polymer properties. The crosslinking of polyolefins, especially of polyethylene, can be achieved by incorporating in the polymer a relatively stable peroxide such as dicumyl peroxide, followed by the heating of the polymer, which leads to a vulcanization type process. The decomposition of the peroxide forms bridges across the polyethylene chain and gives a stronger material.

Thermal decomposition of polyolefins typically starts with a random scission continuing with the formation of a variety of alkenes, alkanes, and alkadienes. Pyrolysis at temperatures higher than 600°C also gives some dehydrogenation. Only at temperatures higher than $700\text{--}800^\circ\text{C}$ does the formation of aromatic hydrocarbons begin to be noticeable. For the polyolefins with longer side chains, the compounds formed in the fragmentation occur in both the backbone and in the side chain. Details on pyrolysis of several individual polymers from this class are discussed below.

- Polyethylene

Polyethylene (PE), CAS# 9002-88-4, is a common polymer with numerous practical utilizations. The polymer is available in several forms, two of them being the most common. One is the low-density or branched polyethylene (LDPE) [1], and the other is high-density or linear polyethylene (HDPE). Medium-density polyethylenes also are known, having a structure of the type $[-(\text{CH}_2\text{CH}_2)_x\text{-(branched hydrocarbon)}-(\text{CH}_2\text{CH}_2)_y]\text{-}$. Low-density polyethylene is typically obtained from ethylene at high pressure in the

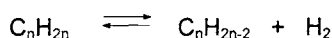
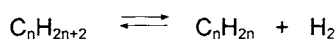
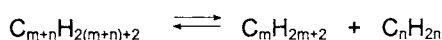
presence of traces of oxygen. The branching of the polymer occurs probably because of intermolecular hydrogen transfer reactions during the polymerization process. The branching includes short-chain branching and long chain branching. Short-chains include mostly ethyl (C_2), butyl (C_4), and amyl (C_5). Other short chains such as methyl (C_1), propyl (C_3), or larger than hexyl are less common.

The high-density polymer is virtually linear and can be obtained from ethylene using a coordination type catalyst (alkyl aluminum and $TiCl_4$) or by polymerization on a metal oxide catalyst. The structure of both polymers is usually indicated by the structure $(-CH_2CH_2-)_n$, although the branching in the low density polymer implies the presence of $-CH<$ groups. The same type of bonds may be present in crosslinked polyethylene.

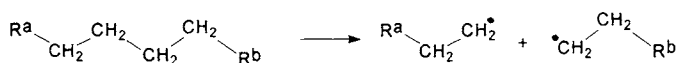
The study of polyethylene thermal decomposition is important in relation to the polymer resistance to heating [2], to various attempts to use waste containing polyethylene as a combustible or as a source of other useful materials [3–7], or to environmental issues when polyethylene is burned [8]. Various other studies on polyethylene pyrolysis were reported [9–22], etc.

Numerous studies have been performed on polyethylene pyrolysis [22–41]. These studies include flash pyrolysis in He, in air, in the presence of various catalysts, in the presence of steam, under pressure, etc. Also, besides analytical pyrolysis, some of the studies were performed at slow heating rates that better simulate pyrolysis in industrial incinerators. Most frequently, the analysis of polyethylene pyrolysates has been done using GC/MS. However, other techniques also were applied, such as pyrolysis field ionization mass spectrometry [42].

Thermal decomposition of polyethylene in an inert atmosphere starts at about $280^\circ C$ and occurs mainly following fragmentation and dehydrogenation reactions, the fragmentation being predominant at temperatures below $600^\circ C$ (see Section 2.2). Hydrocarbons, from 2 carbon atoms up to 90 carbons, were identified in pyrolysates. Three types of fragment molecules are the most common, namely alkenes, alkanes, and α,ω -dienes. Traces of other hydrocarbons also are formed during pyrolysis. Some reactions typical for polyethylene pyrolysis are shown below:



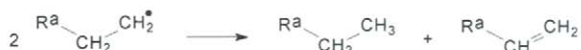
The mechanism of thermal decomposition for polyethylene starts with a random scission as follows:



The propagation reaction leading to new polymeric radical chains and smaller stable molecules can take place through reactions of the following type:



The termination reaction also generates stable molecules, for example by disproportionation with the generation of an alkane and of an α -olefin:



The elimination of ethylene (the monomer) is not favored energetically, and pyrolysis of polyethylene does not occur as an unzipping process. Dienes are formed during pyrolysis by the same process as described above, with an α -olefin undergoing the cleavage followed by the radical disproportionation with the formation of an α,ω -diene. At higher temperatures, above 700–800° C, traces of polycyclic aromatic hydrocarbons (PAHs) are formed in the pyrolysis process [43, 44]. The variation in the level of several PAHs generated in a pyrolysis experiment in which 50 mg PE was introduced in a preheated oven at different temperatures are shown in Figure 6.1.1 [43].

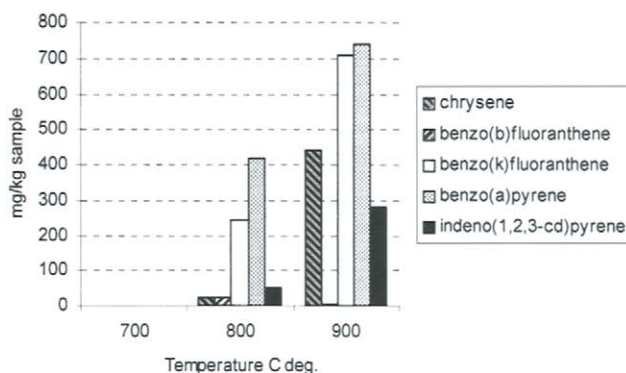


FIGURE 6.1.1. Production in mg/kg sample of several PAHs as a function of temperature during PE pyrolysis [43].

The kinetics of polyethylene pyrolysis has been studied frequently [45–52]. It was shown that random scission degradation of polyethylene does not follow rigorously first-order kinetics. The reaction order of the dynamic degradation as well as of isothermal degradation of a high-density polyethylene was determined to be 0.55 [53]. The thermal decomposition of polyethylenes with different characteristics (i.e. density or melt flow index) showed no significant differences in the thermal decomposition process when no catalyst was used, while in the presence of a solid acid catalyst, considerable differences in the decomposition temperatures were found [54]. A number of fragment molecules are generated from polyethylene thermal decomposition. For high-density polyethylene heated between 335° C and 450° C, the fragment molecules include

saturated and mono and di-unsaturated hydrocarbons from C_2 - C_{90} . Lower heating temperature was found to favor the formation of larger fragments [55, 56]. For low-density polyethylene, the result is similar; heated from ambient to 500° C, traces of hydrogen and a range of saturated and mono and di-unsaturated hydrocarbons C_1 - C_{40} are obtained [57].

The results for a Py-GC/MS analysis of a high-density polyethylene sample are shown in Figure 6.1.2. The pyrolysis was done at 600° C in He at a heating rate of 20° C/ms with 10 s THT. The separation was done on a Carbowax column (60 m, 0.32 mm i.d., 0.32 μ m film thickness) with the GC starting at 40° C with a ramp of 2° C/min. up to 240° C and a final oven time of 20 min., as also described in table 4.2.2. The MS was operated in EI+ mode. The peak identification for the chromatogram shown in Figure 6.1.2 was done using MS spectral library searches and is given in Table 6.1.1. The spectra for most of the compounds from polyethylene pyrolysate are available in common commercial mass spectral libraries (NIST 2002, Wiley 7, or earlier versions of these).

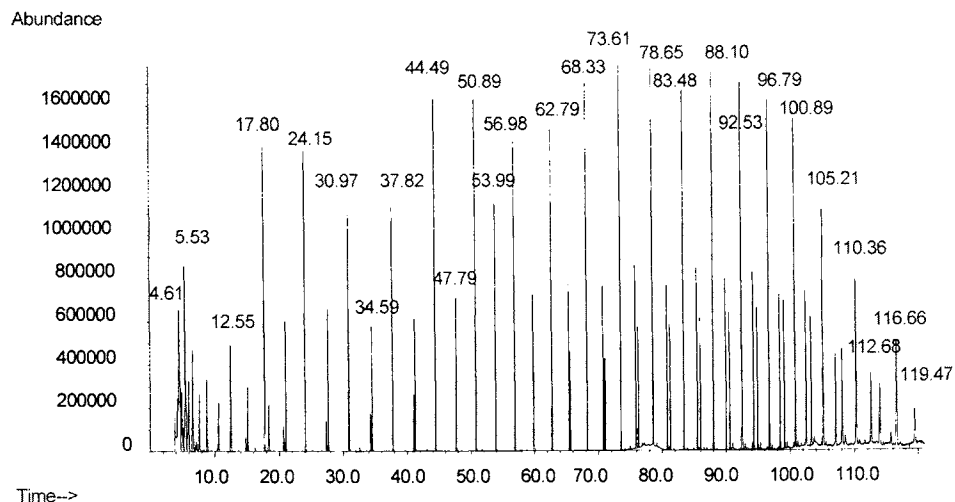


FIGURE 6.1.2. Pyrogram from a Py-GC/MS analysis of high-density polyethylene. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 6.1.1. Compounds identified in the pyrogram of high-density polyethylene shown in Figure 6.1.2.

Peak	Type*	Compound	Ret. Time	MW**	Area %
1	C3;1:1	propene	4.61	42	4.69
2	C4;1:1	1-butene	4.75	56	trace
3	C5;1:1	1-pentene	4.96	70	0.88
4	C6;0	hexane	5.22	86	0.53
5	C6;1:1	1-hexene	5.53	84	2.61
6	C5;2:1,3	2-methyl-1,3-butadiene	5.86	68	trace
7	C7;0	heptane	6.03	100	1.69
8	C7;1:1	1-heptene	6.67	98	1.48
9		methylcyclohexane	7.27	98	trace
10	C8;0	octane	7.68	114	1.02
11	C8;1:1	1-octene	8.85	112	1.05
12	C9;0	nonane	10.65	128	1.11
13	C9;1:1	1-nonene	12.55	126	1.24
14	C9;2:1,8	1,8-nonadiene	14.88	124	0.20
15	C10;0	decane	15.21	142	0.76
16	C10;1:1	1-decene	17.80	140	2.49
17		water	18.48	18	0.46
18	C10;2:1,9	1,9-decadiene	20.75	138	0.23
19	C11;0	undecane	21.09	156	1.12
20	C11;1:1	1-undecene	24.15	154	2.20
21	C11;2:1,10	1,10-undecadiene	27.42	152	0.29
22	C12;0	dodecane	27.75	170	1.11
23	C12;1:1	1-dodecene	30.97	168	1.68
24	C12;2:1,11	1,11-dodecadiene	34.31	166	0.34
25	C13;0	tridecane	34.59	184	0.96
26	C13;1:1	1-tridecene	37.82	182	1.40
27	C13;2:1,12	1,12-tridecadiene	41.04	180	0.32
28	C14;0	tetradecane	41.31	198	1.42
29	C14;1:1	1-tetradecene	44.49	196	2.38
30	C14;2:1,13	1,13-tetradecadiene	47.55	194	trace
31	C15;0	pentadecane	47.79	212	1.64
32	C15;1:1	1-pentadecene	50.89	210	2.40
33	C16;0	hexadecane	53.99	226	1.79
34	C15;2:1,14	1,14-pentadecadiene	54.00	208	trace
35	C16;1:1	1-hexadecene	56.99	224	2.31
36	C17;0	heptadecane	59.89	240	1.23
37	C16;2:1,15	1,15-hexadecadiene	59.96	222	0.50
38	C17;1:1	1-heptadecene	62.79	238	2.16
39	C18;0	octadecane	65.51	254	1.27
40	C17;2:1,16	1,16-heptadecadiene	65.70	236	0.74
41	C18;1:1	1-octadecene	68.33	252	2.56
42	C19;0	nonadecane	70.87	268	1.37
43	C18;2:1,17	1,17-octadecadiene	71.15	250	0.84
44	C19;1:1	1-nonadecene	73.61	266	2.74
45	C20;0	n-eicosane	75.99	282	1.56
46	C19;2:1,18	1,18-nonadecadiene	76.34	264	0.96

* The notation C_x;y:z,w indicates by x the number of carbon atoms, by y the number of double bonds, by z,w the position(s) of double bonds in the molecule.

** The masses shown in Table 6.1.1 and other similar tables in this book represent only the mass obtained from the most abundant isotopes rounded to the unit. This mass is typically used for MS interpretations [58].

TABLE 6.1.1 (continued). Compounds identified in the pyrogram of high-density polyethylene shown in Figure 6.1.2.

Peak	Type	Compound	Ret. Time	MW	Area %
47	C20;1:1	eicos-1-ene	78.65	280	2.63
48	C21;0	heneicosane	80.88	296	1.34
49	C20;2:1,19	1,19-eicosadiene	81.31	278	1.02
50	C21;1:1	1-heneicosene	83.48	294	2.54
51	C22;0	n-docosane	85.57	310	1.43
52	C21;2:1,20	1,20-heneicosadiene	86.06	292	1.03
53	C22;1:1	1-docosene	88.10	308	2.72
54	C23;0	n-tricosane	90.06	324	1.32
55	C22;2:1,21	1,21-docosadiene	90.62	306	1.11
56	C23;1:1	1-tricosene	92.53	322	2.96
57	C24;0	n-tetracosane	94.38	338	1.38
58	C23;2:1,22	1,22-tricosadiene	94.99	320	1.07
59	336	1-tetracosene	96.79	336	2.44
60	C25;0	n-pentacosane	98.52	352	1.33
61	C24;2:1,23	1,23-tetracosadiene	99.19	334	1.32
62	C25;1:1	1-pentacosene	100.89	350	4.06
63	C26;0	n-hexacosane	102.57	366	2.14
64	C25;2:1,24	1,24-pentacosadiene	103.36	348	1.31
65	C26;1:1	1-hexacosene	105.21	364	2.04
66	C27;0	n-heptacosane	107.16	380	1.00
67	C26;2:1,25	1,25-hexacosadiene	108.18	362	1.00
68	C27;1:?	heptacosene (isomer)	110.12	378	0.19
69	C27;1:1	1-heptacosene	110.36	378	1.69
70	C28;0	n-octacosane	112.68	394	0.80
71	C27;2:1,26	1,26-heptacosadiene	114.02	376	0.67
72	C28;1:1	1-octacosene	116.66	392	1.30
73	C29;0	n-nonacosane	119.47	408	0.59

Some spectra for common hydrocarbons with a larger number of carbons are not always available. As an example, the spectrum of n-heptacosane is available in common mass spectral libraries, but 1-heptacosene, and 1,26-heptacosadiene are not. The spectra of C27 hydrocarbons n-heptacosane, and 1-heptacosene are shown in Figure 6.1.3 a, and that of 1,26-heptacosadiene is shown in Figure 6.1.3 b. For many of the hydrocarbons given in Table 6.1.1, the molecular ion is present in the mass spectrum.

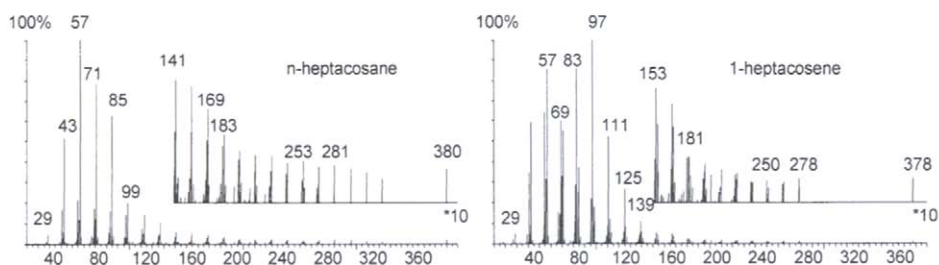


FIGURE 6.1.3 a. Mass spectra of n-heptacosane (MW = 380) (available in mass spectral libraries) and that of 1-heptacosene (MW = 378).

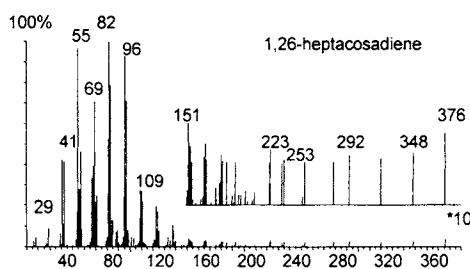


FIGURE 6.1.3 b. Mass spectrum of 1,26-heptacosadiene (MW = 376).

As seen in Table 6.1.1, compounds only up to C₂₉ are seen in previously described experimental conditions. In fact, compounds with higher number of carbons also are generated during pyrolysis. The limitation to C₂₉ is caused by the lower volatility of higher molecular mass compounds, which are not eluted from a Carbowax column heated only up to 240° C. In different chromatographic conditions, up to C₉₀ alkanes, alkenes and alkadienes can be seen. Water, which generates a peak in the chromatogram from Figure 6.1.2, is probably the result of the external contamination of the polymer. The presence of numerous peaks of about the same intensity in the pyrogram is an indication of the random scission mechanism of the pyrolysis process and the equal stability of the molecules with different numbers of carbon atoms. The presence of alkanes, alkenes, and dienes shows that the process is terminated by disproportionation when the radical chain is still rather long. The propagation process also may lead to formation of alkenes, since these are the most abundant components in the pyrogram.

The whole chromatogram of PE pyrolysate is basically formed from a series of triplets (alkane, alkene, alkadiene). A narrow time window from 34 to 42 min. of the chromatogram from Figure 6.1.2 is shown in Figure 6.1.4.

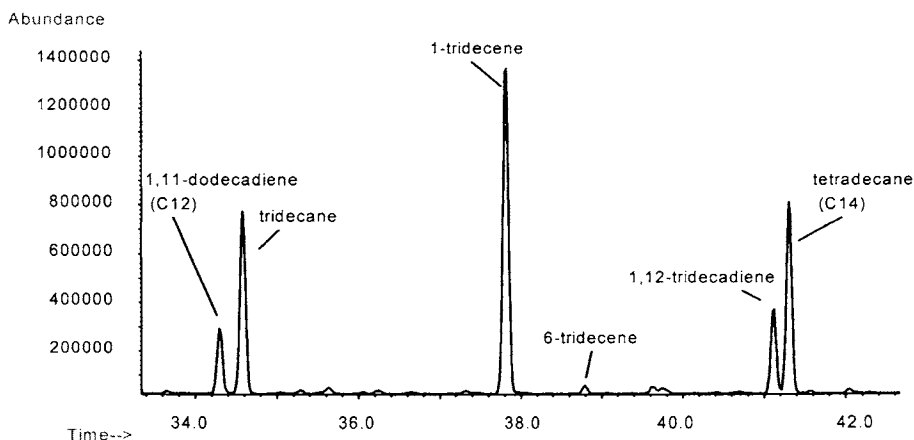


FIGURE 6.1.4. A narrow time window in a pyrogram obtained from high-density polyethylene at 600° C in He, with the separation on a Carbowax type column.

The peaks displayed are tridecane, 1-tridecene and 1,12-tridecadiene. The figure also shows 1,11-dodecadiene, which belongs to the previous set of triplet peaks containing C12, and tetradecane, which belongs to the following set of triplet peaks containing C14. The relative abundance of alkane, alkene and alkadiene in each triplet is dependent on the pyrolysis temperature. As the temperature increases, for each triplet with the given number of carbons, the alkane peak decreases and the alkadiene peak increases [24]. This happens because the dehydrogenation reaction is favored by increased temperatures, as shown theoretically (see Section 2.2) and also proven experimentally by the increased hydrogen content of the pyrolysate [29]. The heating rate during pyrolysis also influences the alkane vs. alkadiene ratios in each triplet, a higher heating rate favoring the formation of the diene. Pyrolysis of low-density polyethylene compared to that of high-density polyethylene does not show significant differences regarding the main components, and similar results are obtained for medium-density polyethylene. However, depending on the degree of branching of the polymer, the presence of hydrocarbons with branched molecules can be detected as small components in the pyrogram of low-density polyethylene. Branching was frequently studied using analytical pyrolysis [59, 60]. One procedure that was proven to allow a better way to determine the degree of branching is the use of pyrolysis-hydrogenation GC [61]. In this procedure, the unsaturated hydrocarbons generated during PE pyrolysis are transformed into saturated molecules such that the pyrogram is simplified and only the differences between structural isomers are seen. By estimating the content of isomers for each linear alkane, it is possible to estimate with good precision the degree of branching.

The differences between low and high-density polyethylene in a Py-GC/MS experiment without hydrogenation is exemplified in Figure 6.1.5.

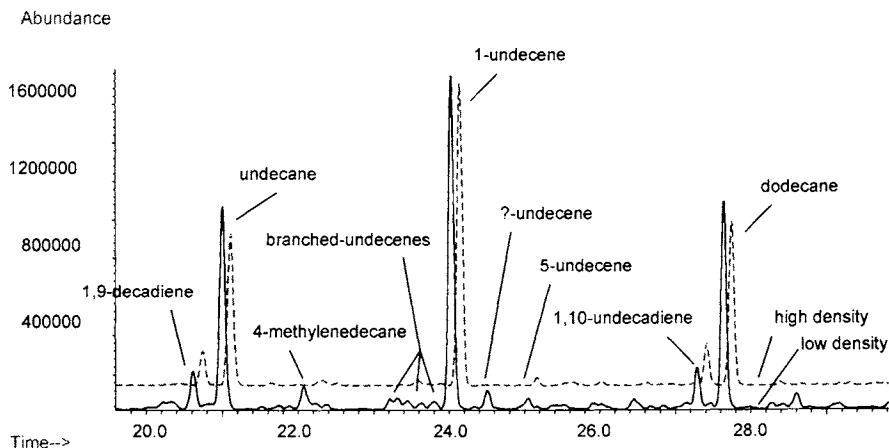


FIGURE 6.1.5. A time window between 20 and 30 min. showing pyrograms obtained from high-density polyethylene and low-density polyethylene at 600° C in He, with the separation on a Carbowax type column.

This figure shows a time window between 20 and 30 min. in a pyrogram of high-density polyethylene (upper trace) and of low-density polyethylene (lower trace). The lower trace has more peaks of branched fragment molecules. The main peaks in the window consisting of 1,9-decadiene, undecane, 1-undecene, 1,10-undecadiene, and dodecane are the same for the two types of polyethylene. Pyrolysis of polyethylene in air performed at high heating rates such as 20° C/ms does not show significant differences compared to pyrolysis in He. On the other hand, with the heating rate as low as 30° C/s, compounds such as alcohols and aldehydes are formed and seen in pyrograms, and the peak intensities of hydrocarbons are significantly decreased. Since during the pyrolysis in air the oxidation and pyrolysis are competing processes, the extent of oxidation is also conditioned by the rate of access of oxygen to the sample. For this reason, the instrumentation as well as the amount and shape of the sample play a role in the extent of the oxidation process. Some molecules resulting from the thermal decomposition of low-density polyethylene in air between 264° C and 289° C include CO₂, H₂O, ethene, propene, propane, cyclopropane, butene, butane, pentene, pentane, hexene, hexane, heptene, heptane, octene, octane, methanol, ethanol, furan, tetrahydrofuran, formaldehyde, acetaldehyde, propanal, acrolein, butanal, isobutanal, pentanal, acetone, methyl vinyl ketone, methyl ethyl ketone, 2-pentanone, 2-hexanone, 2-heptanone, formic acid, acetic acid, propionic acid, acrylic acid, butyric acid, isovaleric acid, hydroxyvaleric acid, crotonic acid, caproic acid, butyrolactone, and valerolactone [62].

Pyrolysis of polyethylene on catalysts of metal-supported activated carbon changes the composition of pyrolysates with the formation of aromatic compounds. Different metals lead to different yield of aromatic components, the presence of Pt leading to the highest, and Fe and Cu leading to the lowest content of aromatics [63].

Polyethylene samples may have in some cases structural differences generated either by the variation in the production procedure, by the addition of a small amount of other monomers (1–2 mol %) during the polymerization process (and formation of a copolymer), by the addition of polymerization inhibitors (terminators), or by the presence of additives. The main pyrolysis products of the polymer remain the same. However, some details in the pyrograms can be different. For example, medium-density polyethylene can be obtained by mixing LDPE and HDPE, by forming a copolymer of ethylene with low amounts of a comonomer (1-butene, 1-hexene, or 1-octene), or by controlling the degree of polymerization with terminators. Different medium-density polyethylenes upon pyrolysis may generate minor constituents indicative of their manufacturing path. As an example, the pyrogram of a sample of medium-density polyethylene is shown in Figure 6.1.6. The pyrogram was obtained in similar conditions as that for high-density polyethylene. The main peaks in the pyrogram from Figure 6.1.6 are the same as those shown in Figure 6.1.2. Small variations in the retention times are caused by the variability in the chromatographic separation, but each peak can be matched easily with the list given in Table 6.1.1. However, the pyrogram of the polymer shown in Figure 6.1.6 has a number of additional peaks that are not hydrocarbons. These peaks are not present in pure polyethylene and have the characteristic ion $m/z = 59$.

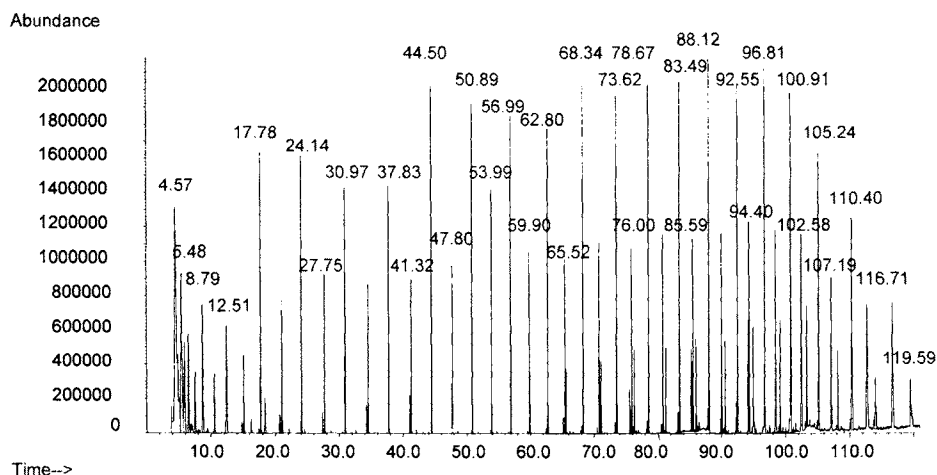


FIGURE 6.1.6. Result for a Py-GC/MS analysis of medium-density polyethylene. Pyrolysis done at 600° C in He, with the separation on a Carbowax type column.

From the pyrogram given in Figure 6.1.6, the extracted ion chromatogram for the ion $m/z = 59$ is shown in Figure 6.1.7. This ion is absent in the spectra of hydrocarbon type compounds shown in Table 6.1.2. The identification of the peaks containing the ion with $m/z = 59$, done using MS library search, is indicated in Table 6.1.2.

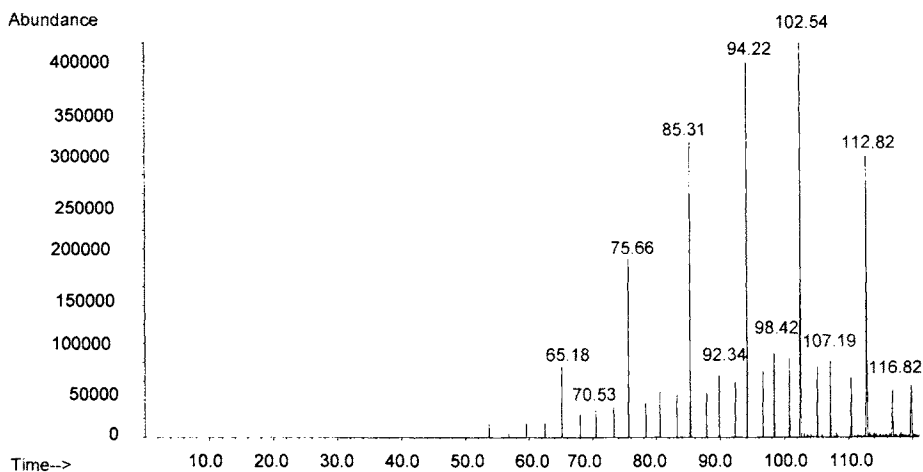


FIGURE 6.1.7. Extracted ion $m/z = 59$ for the pyrogram of an impure medium-density polyethylene sample. The TIC for the same sample is shown in Figure 6.1.6. Pyrolysis done at 600° C in He, with the separation on a Carbowax type column.

TABLE 6.1.2. Compounds containing the ion $m/z = 59$ identified in an impure polyethylene sample.

Peak	Compound	Ret. Time	MW	*Area %
1	2-methyl-2-propanol	11.04	74	0.02
2	2-methyl-2-butanol	16.39	88	0.02
3	2-methyl-3-buten-2-ol	17.96	86	0.01
4	2-methyl-2-pentanol	21.71	102	0.03
5	2-methyl-4-penten-2-ol	22.86	100	0.03
6	2-methyl-2-hexanol	28.15	116	0.05
7	2-methyl-5-hexene-2-ol	32.04	114	0.04
8	2-methyl-2-heptanol	34.67	130	0.07
9	2-methyl-6-heptene-2-ol	38.39	128	0.07
10	2-methyl-2-octanol	41.30	144	0.07
11	2-methyl-7-octene-2-ol	44.53	142	0.08
12	2-methyl-2-nonanol	47.65	158	0.09
13	2-methyl-8-nonene-2-ol	50.90	156	0.09
14	2-methyl-2-decanol	53.75	172	0.12
15	2-methyl-9-decene-2-ol	56.85	170	0.10
16	2-methyl-2-undecanol	59.59	186	0.12
17	2-methyl-10-undecene-2-ol	62.56	184	0.13
18	2-methyl-2-dodecanol	65.18	200	0.23
19	2-methyl-11-dodecene-2-ol	68.07	198	0.14
20	2-methyl-2-tridecanol	70.53	214	0.14
21	2-methyl-12-tridecene-2-ol	73.32	212	0.15
22	2-methyl-2-tetradecanol	75.66	228	0.49
23	2-methyl-13-tetradecene-2-ol	78.37	226	0.16
24	2-methyl-2-pentadecanol	80.58	242	0.18
25	2-methyl-14-pentadecene-2-ol	83.21	240	0.18
26	2-methyl-2-hexadecanol	85.31	256	0.74
27	2-methyl-15-hexadecene-2-ol	87.87	254	0.23
28	2-methyl-2-heptadecanol	89.85	270	0.34
29	2-methyl-16-heptadecene-2-ol	92.34	268	0.34
30	2-methyl-2-octadecanol	94.22	284	1.18
31	2-methyl-17-octadecene-2-ol	96.65	282	0.32
32	2-methyl-2-nonadecanol	98.42	298	0.37
33	2-methyl-18-nonadecene-2-ol	100.80	296	0.52
34	2-methyl-2-eicosanol	102.54	312	1.39
35	2-methyl-19-eicosene-2-ol	105.18	310	0.67
36	2-methyl-2-heneicosanol	107.19	326	0.68
37	2-methyl-20-heneicosene-2-ol	110.41	324	0.53
38	2-methyl-2-docosanol	112.82	340	1.57
39	2-methyl-21-docosene-2-ol	116.82	338	0.58
40	2-methyl-2-tricosanol	119.77	356	1.15

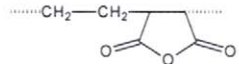
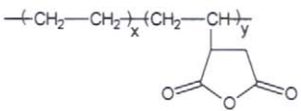
* The area percent in Table 6.1.2 is given based on the areas for the TIC of all peaks in the chromatogram shown in Figure 6.1.6.

The compounds shown in Table 6.1.2 are indicative of the presence of $-\text{C}(\text{CH}_3)_2\text{OH}$ groups in the polymer structure.

- Copolymers of ethylene

Ethylene is used in a considerable number of copolymers. Some of these are binary copolymers, but copolymers of three or even four components also are known. As indicated in Section 2.3, specific monomer reactivity ratios are required for generating a copolymer. However, this requirement is satisfied for a number of monomers. Some common copolymers of polyethylene are indicated in Table 6.1.3. Some of the copolymers listed in Table 6.1.3 are *alt*-copolymers. They behave during pyrolysis as homopolymers. More details regarding pyrolysis of several *alt*-copolymers are given further in this section for poly(propylene-*alt*-ethylene), in Section 6.3 for poly(ethylene-*alt*-chlorotrifluoroethylene), and in Section 6.9 for poly(ethylene-*alt*-maleic anhydride). The copolymers in which the backbone chain contains atoms different from carbon, such as oxygen or sulfur, are discussed in sections dedicated to polymers containing that particular atom in the backbone.

TABLE 6.1.3. Common copolymers of ethylene

Copolymer name	CAS #	Structure
poly(ethylene- <i>alt</i> -chlorotrifluoroethylene)	25101-45-5	$[-CH_2CH_2-CF(Cl)CF_2-]_n$
poly(ethylene- <i>alt</i> -maleic anhydride)	9006-26-2	
poly(propylene- <i>alt</i> -ethylene)	127883-08-3	$[-CH(CH_3)-CH_2CH_2CH_2-]_n$
poly(chloroethene-co-ethene)	25037-78-9	$(-CH_2CH_2-)_x(-CH_2CH(Cl)-)_y$
poly(ethylene-co-acrylic acid)	9010-77-9	$(-CH_2CH_2-)_x(-CH_2CH(COOH)-)_y$
poly(ethylene-co-butyl acrylate)		$(-CH_2CH_2-)_x[-CH_2CH(COOC_4H_9)-]_y$
poly(ethylene-co-carbon monoxide)	25052-62-4	$(-CH_2CH_2-)_x(-CO-)_y$
poly(ethylene-co-ethyl acrylate)	9010-86-0	$(-CH_2CH_2-)_x[-CH_2CH(COOC_2H_5)-]_y$
poly(ethylene-co-methacrylic acid salt)	25608-26-8	$(-CH_2CH_2-)_x[-CH_2C(CH_3)(COONa)-]_y$
poly(ethylene-co-methacrylic acid)	25053-53-6	$(-CH_2CH_2-)_x[-CH_2C(CH_3)(COOH)-]_y$
poly(ethylene-co-methyl acrylate)	25103-74-6	$(-CH_2CH_2-)_x[-CH_2CH(COOCCH_3)-]_y$
poly(ethylene-co-propylene)	25038-36-2, etc.	$(-CH_2CH_2-)_x[-CH_2CH(CH_3)-]_y$
poly(ethylene-co-sulfur dioxide)	29085-22-5	$(-CH_2CH_2-)_x(-SO_2-)_y$
poly(ethylene-co-vinyl acetate)	24937-78-8	$(-CH_2CH_2-)_x[-CH_2CH(OOCCH_3)-]_y$
poly(ethylene-co-vinyl alcohol)	25067-34-9	$(-CH_2CH_2-)_x[-CH_2CH(OH)-]_y$
poly(ethylene- <i>graft</i> -maleic anhydride)	106343-08-2	
polyethylene- <i>block</i> -poly(ethylene glycol)	97953-22-5	$CH_3CH_2(-CH_2CH_2-)_x(-OCH_2CH_2-)_yOH$
poly(propylene-co-ethylene-co-butylene)	25895-47-0	$[-CH_2CH(CH_3)-]_x[-CH_2CH_2-]_y$ $[-CH_2CH(CH_2CH_3)-]_z$
poly(chloroethene-co-ethene-co-ethenyl acetate)	25085-46-5	$(-CH_2CH_2-)_x(-CH_2CH(Cl)-)_y$ $[-CH_2CH(COOCCH_3)-]_z$
poly(acrylonitrile-co-ethylene-co-propylene-co-styrene) (AES impact modified)		$[-CH_2CH(CN)-]_x[-CH_2CH_2-]_y$ $[-CH_2CH(CH_3)-]_z[-CH_2CH(C_6H_5)-]_w$

Ethylene copolymers have many practical applications. Some copolymers are plastic materials and others are elastomers, which are widely used in cost effective rubber compounding. Over 150 grades are available with applications in automotive industry,

household objects, electrical cable insulation and jacketing, etc. The copolymer with acrylic acid, which can be obtained under high pressure using free radical initiators to produce a highly branched polymer, can be used in coatings (although the carboxylic groups in this copolymer impart some acidity), laminates with paper, metal foils, nylon, polyethylene and polyesters, etc. The copolymer with vinyl alcohol can be used in the formation of film and sheeting material. The product with high ethylene content can be used as adhesive, as coating material, and as an additive for rubber materials. The terpolymer poly(propylene-co-ethylene-co-butylene) is used mainly in the production of film packaging.

Thermal properties of ethylene copolymers are studied frequently and reported in literature [64–70]. These studies were directed to the evaluation of copolymer properties, use of various catalysts for achieving pyrolysis in order to recover polymer waste [71–75]. Some studies on thermal properties of ethylene copolymers are summarized in Table 6.1.4.

TABLE 6.1.4. *Some literature reports regarding thermal behavior of ethylene copolymers [76].*

Polymer	Temp. °C	Results	Ref.
poly(ethylene-co-ethyl acrylate) 18/1 mole ratio	ambient to 500	broad spectrum of saturated and unsaturated hydrocarbons, ethyl esters and carboxylic acids; ethanol, ethylene, CO ₂ , CO and small amounts of ketene and ethyl acrylate	57
poly(ethylene-co-vinyl acetate)	250–400	loss of acetic acid takes place in a first stage followed by the second stage when the backbone scission starts; polyethylene sequences are more stable compared to vinyl acetate ones; the two types of chain units behave independently	66
poly(ethylene-co-vinyl acetate)	350–400	catalytic decomposition on zeolite forms acetic acid, and high selectivity toward C ₁ –C ₅ olefins can be achieved	73
poly(ethylene-co-vinyl acetate) (12–33% mol% vinyl acetate)	ambient to 500	acetic acid, ketene, CO ₂ , ethylene, saturated and unsaturated hydrocarbons, chain fragment fraction containing some vinyl acetate units	77
poly(ethylene-co-vinyl acetate) (38.5 wt. % of ester groups)	260–290	acetic acid > 99%	78
poly(ethylene-co-vinyl alcohol) (32% mol ethylene)	300	2% weight loss	79
poly(ethylene-co-vinyl alcohol) 32% mol ethylene	300	2% weight loss	80
PP/PE/PS/PVC with brominated flame retardant and mixed with poly(ethylene terephthalate) (PET)	430	PET affected significantly the formation of decomposition products and the decomposition behavior of the plastic mixture	75

An example of a pyrogram of a poly(ethylene-co-acrylic acid), CAS# 9010-77-9, that contains 15 wt % acrylic acid is shown in Figure 6.1.8. For comparison, the pyrogram of pure high-density polyethylene is shown together with that of the copolymer (see also Figure 6.1.2.). The pyrolysis was done at 600° C in He with separation of a Carbowax column and MS detection, similarly to other polymers previously discussed in this book (see also Table 4.2.2).

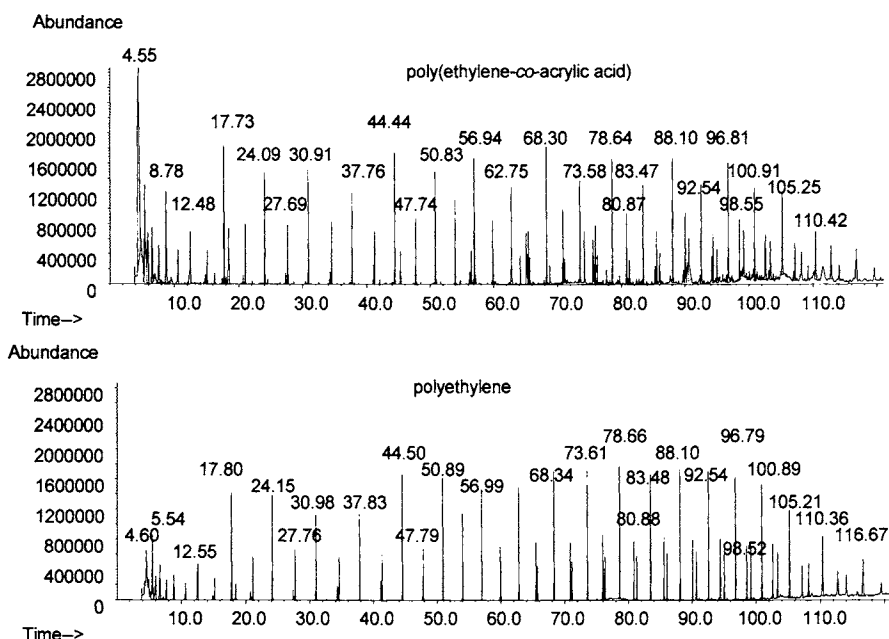


FIGURE 6.1.8. Pyrogram of poly(ethylene-co-acrylic acid) 15% wt. acrylic acid (upper trace) and of high-density polyethylene (lower trace). Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

The molar ratio ethylene/acrylic acid in this polymer is about 1/13, and the peaks generated from the polyethylene segments are very obvious in the pyrogram. Although the polymer is very likely a random polymer, large blocks of polyethylene are present, and probably it should be classified as a block-random copolymer. As a result, and as seen in Figure 6.1.8 or determined if the experimental results are analyzed with data processing capability of a mass spectrometer, the pyrograms of poly(ethylene-co-acrylic acid) and that of polyethylene show many similarities. These similarities are generated by the pyrolysis of polyethylene segments from the copolymer. Individual peak identity can be obtained from Table 6.1.1. Small differences exist in the retention times of the corresponding peaks from the two pyrograms, which are caused by minor variabilities in the chromatographic process. As expected, additional peaks also are present in the pyrogram of the copolymer vs. polyethylene. The larger peaks additional to those already shown in Table 6.1.1 were identified by mass spectral library search and are listed in Table 6.1.5.

TABLE 6.1.5. *Identification of some additional peaks from the pyrolysate of poly(ethylene-co-acrylic acid).* The other peaks in the pyrogram shown in Figure 6.1.8 (upper trace) are identical to those of polyethylene and are identified in Table 6.1.1.

Peak	Compound	Ret. Time	MW	Area %
1	carbon dioxide	4.55	44	13.34
2	3-ethylheptane	9.50	128	trace
3	1,2,3-trimethylcyclopentane	12.31	112	trace
4	6-methyltridecane	17.45	198	trace
5	toluene + 1-butylcyclopentene	18.07	92, 124	trace
6	water	18.49	18	1.51
7	5-methyl-6-methylene-decane	28.66	168	trace
8	3-methyleneundecane	30.44	168	trace
9	2-butyl-1-decene	42.06	196	trace
10	acetic acid	45.30	60	0.61
11	4-methyl-3-pentenoic acid	54.78	114	trace
12	2,4,4-trimethylbut-2-enolide	56.19	126	trace
13	butanoic acid	56.42	88	0.69
14	2-propenoic acid	57.17	72	trace
15	2-butenic acid	62.76	86	1.75
16	pentanoic acid	62.84	102	trace
17	2-ethylbutanoic acid	64.15	116	0.44
18	2-methyl-2-butenic acid	65.11	100	1.41
19	3-nonen-2-one ?	67.85	140	trace
20	hexanoic acid	68.78	116	0.33
21	2-ethylhexanoic acid	74.24	144	0.85
22	2-methyl-2-hexenoic acid	75.61	128	0.95
23	2-heptenoic acid	77.73	128	trace
24	octanoic acid	79.75	144	trace
25	2,5-dimethylheptanoic acid	82.43	158	trace
26	2-methyl-2-hexadecanol	85.28	256	0.25
27	2-methyl-2-pentenoic acid ?	87.66	114	trace
28	2-methyl-3-pentenoic acid ?	89.77	114	trace
29	7,11-dimethyloctadecane	90.40	282	0.72
30	2-methyl-2-octadecanol	94.20	284	0.52
31	2-methyl-2-eicosanol	102.54	312	trace

The area % indicated in Table 6.1.5 is obtained considering all the peaks in the pyrogram and not only those that are listed in the table. Only carbon dioxide is a major peak in the pyrogram generated from the acrylic acid pyrolysis. In addition to that, two types of small components, which are different from those of high-density polyethylene, are seen for the copolymer. One type includes several saturated and unsaturated aliphatic acids (acetic acid to octanoic acid). The other type includes branched hydrocarbons resulting from a less homogeneous polymerization process of ethylene in the presence of acrylic acid. The time window between 60 min. and 80 min. from the pyrograms shown in Figure 6.1.8 is shown in Figure 6.1.9. Other numerous very small peaks present in the pyrogram of the copolymer were not identified, and most of them correspond to branched hydrocarbons.

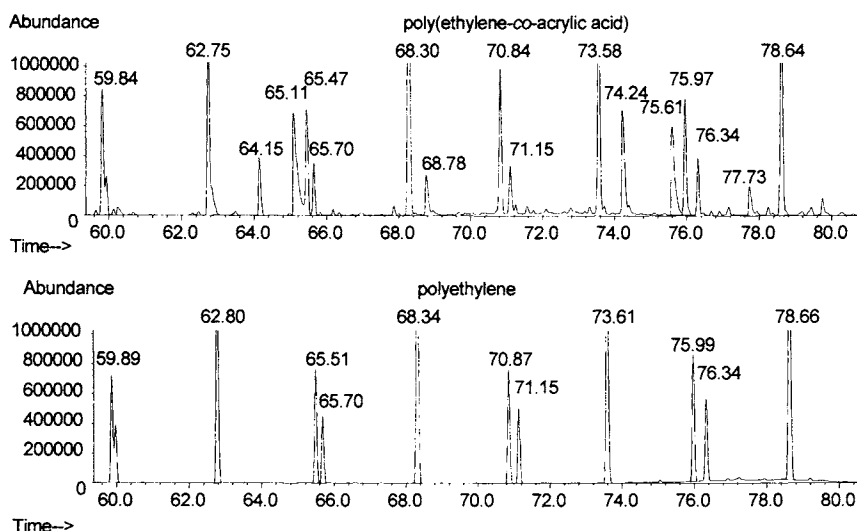
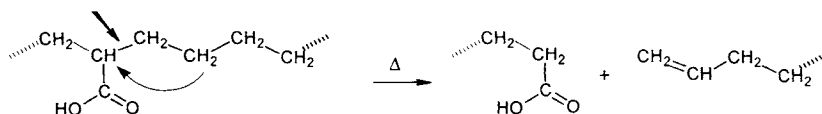
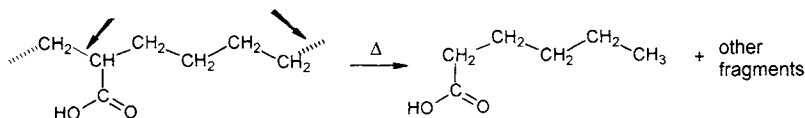


FIGURE 6.1.9. Time window 60 min. to 80 min. from the pyrogram of poly(ethylene-co-acrylic acid) 15% wt. acrylic acid (upper trace) and of high-density polyethylene (lower trace). Whole pyrogram shown in Figure 6.1.8.

The presence of a large content of hydrocarbons including alkanes, alkenes and dienes shows that a significant part of the pyrolytic process leads to the cleavage of the C—C bonds present in the polyhydrocarbon segments or between the hydrocarbon segments and the carbon bearing a carboxyl group as shown below:



Some of the carboxyl groups present in the polymer generate CO_2 . The remaining carboxyl groups may generate the aliphatic carboxylic acids including C1 to C8 as far as they were identified in the pyrogram. The formation of these acids can be explained easily by reactions of the type:



The frequency (area percent) of acids generated in the pyrogram is related to the copolymer structure (see Section 4.1). However, the considerable extent of decarboxylation makes the task of detecting the frequency of alternative groups more difficult compared to the case of other polymers.

Pyrolysis of poly(ethylene-co-methacrylic acid) (10% wt. methacrylic acid), CAS# 25053-53-6, also is dominated by the pyrolysis products of polyethylene. The pyrogram of this copolymer obtained at 600° C in He with separation of a Carbowax column is given in Figure 6.1.10, and for comparison, the pyrogram for polyethylene is shown in the same figure.

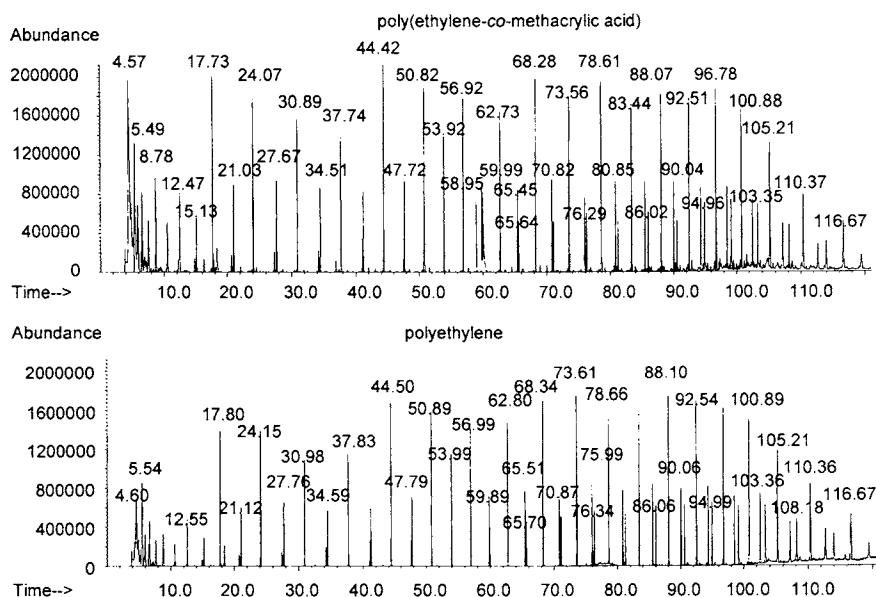


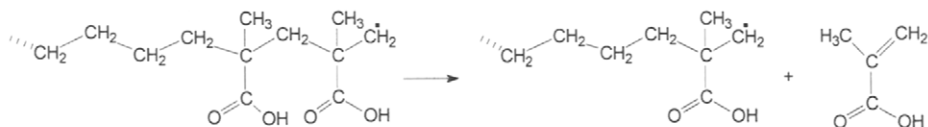
FIGURE 6.1.10. Pyrogram of poly(ethylene-co-methacrylic acid) 10% wt. methacrylic acid (upper trace) and of high-density polyethylene (lower trace). Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

In addition to the peaks generated by polyethylene segments, two larger peaks are generated from the segments of poly(methacrylic acid), one at 58.95 min. belonging to 2-methylbutanoic acid, and one peak at 59.99 min. belonging to the monomer 2-methyl-2-propenoic acid. These peaks represent a larger contribution to pyrolysate than the corresponding acids from the pyrolysate of the copolymer with acrylic acid. In addition to that, traces of some acids with a longer aliphatic chain are seen. These acids and the two main acids resulting from the contribution of methacrylic acid are indicated in Table 6.1.6. A slightly higher abundance of branched hydrocarbons compared to high-density polyethylene also can be noticed in the pyrogram.

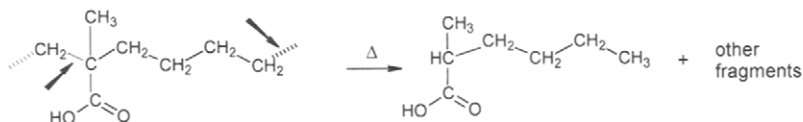
TABLE 6.1.6. Identification of peaks corresponding to compounds bearing carboxyl groups in the pyrolysate of poly(ethylene-co-methacrylic acid).

Peak	Compound	Ret. Time	MW	Area %
1	2-methylbutanoic acid	58.95	102	1.08
2	2-methyl-2-propenoic acid	59.99	86	1.92
3	2-methylpentanoic acid	64.52	116	trace
4	2-methyl-2-butenic acid	68.95	100	trace
5	2-methylhexanoic acid	70.04	130	trace
6	2-methylheptanoic acid	75.40	144	trace
7	2-methyloctanoic acid	80.59	158	trace
8	2-methylnonanoic acid	88.34	172	trace
9	2-methyldecanoic acid	90.25	186	trace
10	2-methylundecanoic acid	94.77	200	trace

From the similarity of the pyrolysis products of the copolymer with that of polyethylene, it can be inferred that the pyrolysis process takes place by a free radical mechanism. The cleavage of the polyethylene segments generates the portion of the pyrolysate identical to that of the polyethylene homopolymer. Similar reactions take place for the poly(methacrylic acid) segments. From a free radical ending with a methacrylic acid unit, the formation of 2-methyl-2-propenoic acid by β -cleavage to the atom bearing the unpaired electrons is shown below:



Acids with longer aliphatic chains are formed in a similar manner, and depending on the hydrogen migration, the resulting acid is saturated or unsaturated. Formation of 2-methylhexanoic acid is shown schematically below.



When the monomer ratio in a copolymer increases, the contribution to the pyrolysate also increases. However, the yield of different pyrolysis products depends on the nature of the polymer. In addition to quantitative information, as shown in Chapter 4, structural information can be obtained from pyrolysate. One example in this direction is that of a poly(ethylene-co-methyl acrylate), CAS# 25103-74-6, (with butylated hydroxyethylbenzene inhibitor). A sample with 21.5% wt. methyl acrylate (MAc), with $M_w = 79,000$ and $M_n = 15,000$, pyrolyzed at 600°C in He with the separation on a Carbowax column generates the upper trace of the two pyrograms shown in Figure 6.1.11. The lower trace, displayed for comparison, is that of polyethylene. The peak identification for the pyrogram of poly(ethylene-co-methyl acrylate), with 21.5% wt. methyl acrylate, shown in Figure 6.1.11 was done using mass spectral library searches only, and is given in Table 6.1.7.

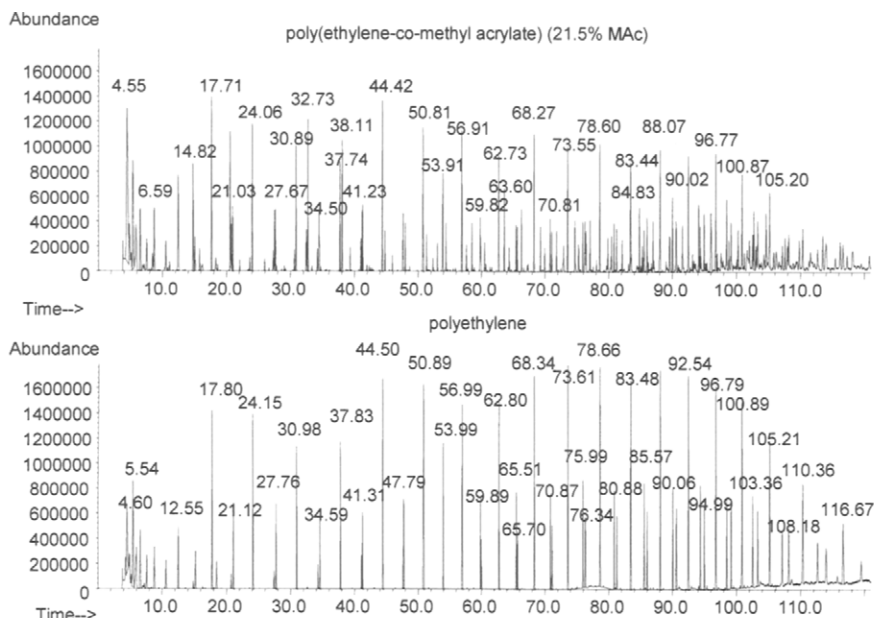


FIGURE 6.1.11. Pyrogram of poly(ethylene-co-methyl acrylate) 21.5% wt. methyl acrylate (upper trace) ($M_w = 79,000$) and of high-density polyethylene (lower trace). Pyrolysis done on 0.4 mg material at 600°C in He, with the separation on a Carbowax type column.

The peaks resulting from the polyethylene segments are hydrocarbons identified by type, similar to those indicated in Table 6.1.1. For comparison, the pyrogram of a poly(methyl acrylate) sample is discussed in Section 6.7 (see Figure 6.7.7 and Table 6.7.5).

TABLE 6.1.7. Identification of peaks in the pyrogram of poly(ethylene-co-methyl acrylate) 21.5% wt. methyl acrylate, $M_w = 79,000$, as shown in Figure 6.1.11 upper trace.

Peak	Type	Compound	Ret. time	MW	Area %
1		carbon dioxide	4.55	44	5.78
2	C5;1:1	1-pentene	4.89	70	1.10
3	C6;0	hexane	5.13	86	0.36
4	C6;1:1	1-hexene	5.45	84	2.72
5	C5;2:1,3	2-methyl-1,3-butadiene	5.78	68	0.22
6	C7;0	heptane	5.94	100	1.05
7	C7;1:1	1-heptene	6.59	98	1.34
8	C8;0	octane	7.59	114	0.64
9		acetic acid methyl ester	8.48	74	0.32
10	C8;1:1	1-octene	8.76	112	1.22
11	C9;0	nonane	10.56	128	0.50
12		propanoic acid methyl ester	11.12	88	0.13
13	C9;1:1	1-nonene	12.48	126	1.84

TABLE 6.1.7 (continued). *Identification of peaks in the pyrogram of poly(ethylene-co-methyl acrylate) 21.5% wt. methyl acrylate, $M_w = 79,000$, as shown in Figure 6.1.11 upper trace.*

Peak	Type	Compound	Ret. time	MW	Area %
14		butanoic acid methyl ester	14.83	102	1.60
15	C10;0	decane	15.12	142	0.42
16		2-methyl-2-propenoic acid methyl ester	15.83	100	0.30
17	C10;1:1	1-decene	17.71	140	2.27
18		water	18.34	18	0.23
19		2-methylenebutanoic acid methyl ester	20.61	114	1.96
20		pentanoic acid methyl ester	20.79	116	0.53
21	C11;0	undecane	21.03	156	0.72
22		2-butenic acid methyl ester	22.10	100	0.13
23		4-pentenoic acid methyl ester	23.66	114	0.15
24	C11;1:1	1-undecene	24.06	154	1.68
25		3-hexenoic acid methyl ester	26.00	128	0.13
26	C11;2:1,10	1,10-undecadiene	27.33	152	0.22
27		hexanoic acid methyl ester	27.49	130	0.64
28	C12;0	dodecane	27.67	170	0.64
29		2-methylenepentanoic acid methyl ester	27.86	128	0.00
30		5-hexenoic acid methyl ester	30.61	128	0.22
31	C12;1:1	1-dodecene	30.89	168	1.44
32		2-ethylhexanoic acid methyl ester	32.49	158	0.43
33		2-methylenehexanoic acid methyl ester	32.73	142	1.68
34	C12;2:1,11	1,11-dodecadiene	34.22	166	0.25
35		heptanoic acid methyl ester	34.34	144	0.00
36	C13;0	tridecane	34.50	184	0.90
37	C13;1:1	1-tridecene	37.74	182	1.18
38		6-heptenoic acid methyl ester	38.11	142	1.48
39		2-methyleneheptanoic acid methyl ester	39.38	156	0.23
40	C13;2:1,12	1,12-tridecadiene	41.04	180	0.35
41	C14;0	tetradecane	41.23	198	0.64
42		octanoic acid methyl ester	41.36	158	0.70
43		2-heptenoic acid methyl ester	41.98	142	0.08
44	C14;1:1	1-tetradecene	44.42	196	1.87
45		4-octenoic acid methyl ester	44.81	156	0.43
46		2-methyleneoctanoic acid methyl ester	45.98	170	0.15
47	C14;2:1,13	1,13-tetradecadiene	47.62	194	0.31
48	C15;0	pentadecane	47.71	212	0.64
49		nonanoic acid methyl ester	48.03	172	0.49
50		2-methyl-2-octenoic acid methyl ester	48.73	156	0.00
51	C15;1:1	1-pentadecene	50.81	210	1.62
52		8-nonenoic acid methyl ester	51.38	170	0.38
53		2-methylenenonanoic acid methyl ester	52.39	184	0.16
54		2-butyl-hexanoic acid methyl ester	53.07	186	0.30
55	C16;0	hexadecane	53.91	226	1.08
56	C15;2:1,14	1,14-pentadecadiene	54.00	208	0.00
57		decanoic acid methyl ester	54.42	186	0.49
58	C16;1:1	1-hexadecene	56.91	224	1.49
59		9-decenoic acid methyl ester	57.65	184	0.30
60		2-methylenedecanoic acid methyl ester	58.51	198	0.48
61	C17;0	heptadecane	59.82	240	0.58
62	C16;2:1,15	1,14-hexadecadiene	59.92	222	0.35
63		undecanoic acid methyl ester	60.51	200	0.32
64		pentanedioic acid dimethyl ester	60.73	160	0.10

TABLE 6.1.7 (continued). Identification of peaks in the pyrogram of poly(ethylene-co-methyl acrylate) 21.5% wt. methyl acrylate, $M_w = 79,000$, as shown in Figure 6.1.11 upper trace.

Peak	Type	Compound	Ret. time	MW	Area %
65		2-decenoic acid methyl ester	61.34	184	0.00
66	C17;1:1	1-heptadecene	62.73	238	1.27
67		10-undecenoic acid methyl ester	63.60	198	0.94
68		2-methyleneundecanoic acid methyl ester	64.37	212	0.23
69	C18;0	octadecane	65.45	254	0.47
70	C17;2:1,16	1,16-heptadecadiene	65.64	236	0.47
71		dodecanoic acid methyl ester	66.30	214	0.66
72		unknown acid	67.36		0.07
73	C18;1:1	1-octadecene	68.27	252	1.61
74		11-dodecenoic acid methyl ester	69.28	212	0.48
75		2-methylenedodecanoic acid methyl ester	69.96	226	0.27
76	C19;0	nonadecane	70.81	268	0.57
77	C18;2:1,17	1,17-octadecadiene	71.09	250	0.43
78		tridecanoic acid methyl ester	71.83	228	0.44
79		2,6-di- <i>tert</i> -butyl-4-ethylphenol (inhibitor)	72.93	234	0.46
80	C19;1:1	1-nonadecene	73.55	266	1.43
81		12-tridecenoic acid methyl ester	74.70	226	0.69
82		2-methylenetridecanoic acid methyl ester	75.30	240	0.30
83	C20;0	n-eicosane	75.94	282	0.56
84	C19;2:1,18	1,18-nonadecadiene	76.29	264	0.56
85		1,4-cyclohexanedicarboxylic acid dimethyl ester	76.44	200	0.47
86		tetradecanoic acid methyl ester	77.10	242	0.62
87	C20;1:1	eicos-1-ene	78.61	280	1.54
88		13-tetradecenoic acid methyl ester	79.88	240	0.44
89		2-methylenetetradecanoic acid methyl ester	80.42	254	0.40
90	C21;0	heneicosane	80.84	296	0.53
91	C20;2:1,19	1,19-eicosadiene	81.26	278	0.48
92		pentadecanoic acid methyl ester	82.14	256	0.36
93	C21;1:1	1-heneicosene	83.44	294	1.52
94		14-pentadecenoic acid methyl ester	84.83	254	0.73
95		2-methylenepentadecanoic acid methyl ester	85.32	268	0.28
96	C22;0	n-docosane	85.53	310	0.46
97	C21;2:1,20	1,20-heneicosadiene	86.03	292	0.65
98		hexadecanoic acid methyl ester	86.96	270	0.56
99		methyl ester of a long chain acid	87.11		0.15
100	C22;1:1	1-docosene	88.07	308	1.73
101		15-hexadecenoic acid methyl ester	89.58	268	0.47
102		2-methylenehexadecanoic acid methyl ester	89.94	282	0.00
103	C23;0	n-tricosane	90.02	324	0.95
104	C22;2:1,21	1,21-docosadiene	90.59	306	0.63
105		heptadecanoic acid methyl ester	91.58	284	0.54
106	C23;1:1	1-tricosene	92.51	322	1.50
107		undecanedioic acid dimethyl ester	93.16	244	0.20
108		16-heptadecenoic acid methyl ester	94.12	282	0.81
109	C24;0	n-tetracosane	94.36	338	0.53
110		2-methyleneheptadecanoic acid methyl ester	94.50	296	0.19
111	C23;2:1,22	1,22-tricosadiene	94.96	320	0.72
112		octadecanoic acid methyl ester	96.02	298	1.32
113	C24;1:1	1-tetracosene	96.77	336	1.51
114	C25;0	n-pentacosane	98.48	352	0.00
115		17-octadecenoic acid methyl ester	98.50	296	1.02

TABLE 6.1.7 (continued). *Identification of peaks in the pyrogram of poly(ethylene-co-methyl acrylate) 21.5% wt. methyl acrylate, $M_w = 79,000$, as shown in Figure 6.1.11 upper trace.*

Peak	Type	Compound	Ret. time	MW	Area %
116		2-methyleneoctadecanoic acid methyl ester	98.82	310	0.46
117	C24;2:1,23	1,23-tetracosadiene	99.17	334	0.89
118		nonadecanoic acid methyl ester	100.27	312	0.63
119	C25;1:1	1-pentacosene	100.87	350	1.32
120		tetradecanedioic acid dimethyl ester ?	102.03	286	0.60
121	C26;0	n-hexacosane	102.56	366	0.63
122		18-nonadecenoic acid methyl ester	102.75	310	0.88
123		2-methylenenonadecanoic acid methyl ester	103.07	324	0.46
124	C25;2:1,24	1,24-pentacosadiene	103.35	348	1.04
125		eicosanoic acid methyl ester	104.66	326	1.13
126	C26;1:1	1-hexacosene	105.20	364	1.58
127	C27;0	n-heptacosane	107.17	380	0.51
128		methyl ester of a long chain acid	107.61		0.53
129		2-methyleneeicosanoic acid methyl ester	107.96	338	0.46
130	C26;2:1,25	1,25-hexacosadiene	108.18	362	0.79
131		heneicosanoic acid methyl ester	109.85	340	0.60
132	C27;1:1	1-heptacosene	110.37	378	0.92
133	C28;0	n-octacosane	112.70	394	0.59
134		19-eicosenoic acid methyl ester	113.49	324	0.74
135	C27;2:1,26	1,26-heptacosadiene	114.01	376	0.84
136		docosanoic acid methyl ester	116.21	354	0.63
137	C28;1:1	1-octacosene	116.67	392	0.60

The peaks from the pyrogram of poly(ethylene-co-methyl acrylate) resulting from the polyethylene segments of the copolymer are the same as those resulting from the pyrolysis of polyethylene homopolymer. This indicates that polyethylene forms long uninterrupted chains in the copolymer. On the other hand, neither 2-methylene-pentanedioic acid dimethylester (dimer of methyl acrylate), nor dimethyl 4-(methoxycarbonyl)-2-methyleneheptane-1,7-dioate (trimer of methyl acrylate), which are generated during poly(methyl acrylate) pyrolysis, are detected in the pyrogram of the copolymer. This finding shows that the methyl acrylate units are usually isolated by chains of alkane. On the other hand, a number of long chain aliphatic acids are present in the pyrolysate. This result is consistent with the random structure of the copolymer, no blocks of methyl acrylate being revealed by pyrolysis.

Pyrolysis for a sample of the same type of copolymer but with a lower proportion of methyl acrylate also was performed. The sample contained 6.5% MAc and the pyrolysis and the separation of pyrolysate were performed in the same conditions as for poly(ethylene-co-methyl acrylate) 21.5% Mac. A time window between 30 min. and 50 min. from the pyrograms of the two samples (with 6.5% MAc and with 21.5% MAc) is shown in Figure 6.1.12.

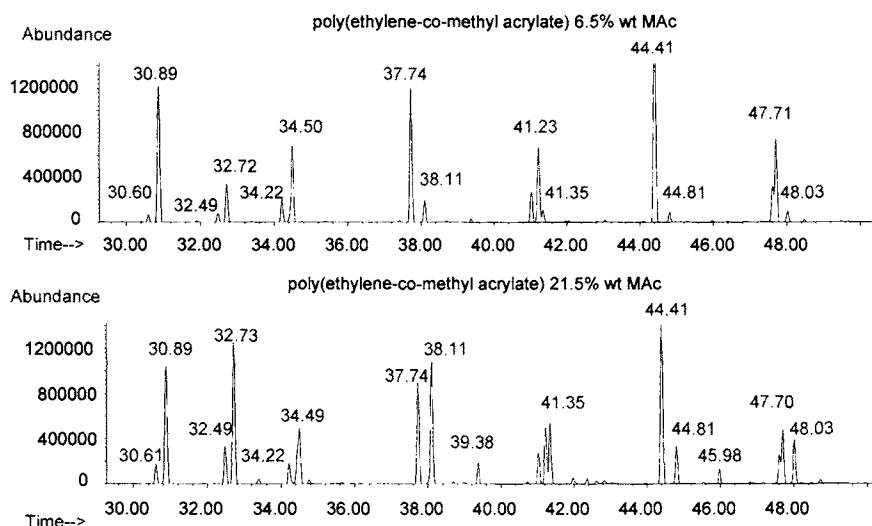


FIGURE 6.1.12. Pyrogram of poly(ethylene-co-methyl acrylate) 6.5% wt. methyl acrylate (upper trace) and of poly(ethylene-co-methyl acrylate) 21.5% wt. methyl acrylate (lower trace). The lower trace is taken from the pyrogram shown in Figure 6.1.11.

The detailed comparison of the two pyrograms shows that the pyrolysis products of the two polymers do not differ in nature. The same fragment molecules seen in the sample with 21.5 % methyl acrylate are seen in that of the sample with 6.5% methyl acrylate. The fragment molecules generated from the polyethylene segments are slightly higher in the 6.5% MAc sample compared to those from the 21.5% MAc sample. The area ratio of many peaks from PE in the two pyrograms is close to 1.2 as expected ($93.5/78.5 \approx 1.2$). More variability is seen for the area ratios of the peaks corresponding to methyl esters, these having a variation between 0.2 and 0.4. The expected ratios should be around 0.3 ($6.5/21.5 \approx 0.3$). This indicates that for this particular copolymer the estimation from pyrolysis data of the content of each monomer is possible. A calibration must be generated for this purpose using selected peaks area ratios. However, the precision of such evaluation is not very high.

The results for a Py-GC/MS analysis of a sample of poly(ethylene-co-vinyl acetate), CAS# 24937-78-8, 9% wt. vinyl acetate (with BHT inhibitor) are shown in Figure 6.1.13. The pyrolysis was done at 600° C in He at a heating rate of 20° C/msec similarly to other previously described experiments (see also Table 4.2.2). The separation was done on a Carbowax column (60 m, 0.32 mm i.d., 0.32 µm film thickness) with the GC starting at 40° C with a ramp of 2° C/min. up to 240° C and a final oven time of 20 min. The pyrogram of this copolymer is almost identical with the pyrogram of polyethylene, except for a large peak belonging to acetic acid. Poly(vinyl acetate) generates some aromatic compounds such as benzene, toluene, naphthalene, indene, etc. Following the elimination of acetic acid, double bonds are formed in the backbone of the polymer. Further breaking of the backbone chain generates aromatic structures (see Section 6.5). Only very low traces of these compounds are seen in the pyrogram of the copolymer.

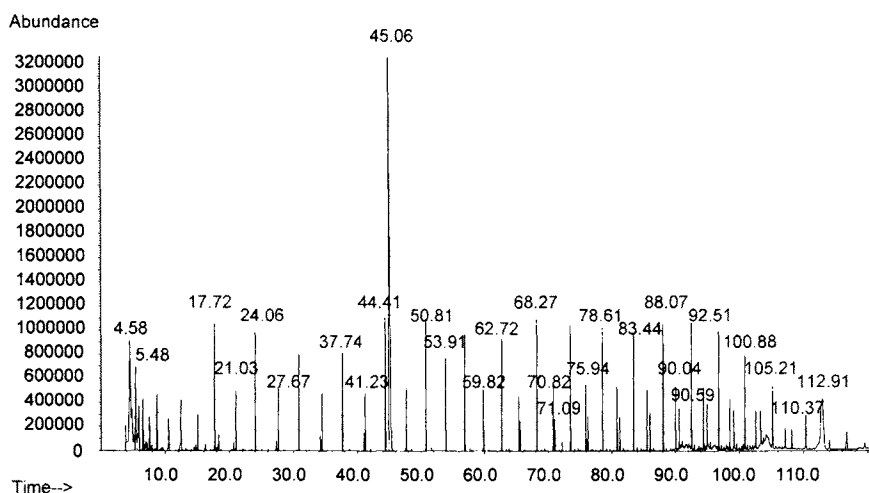
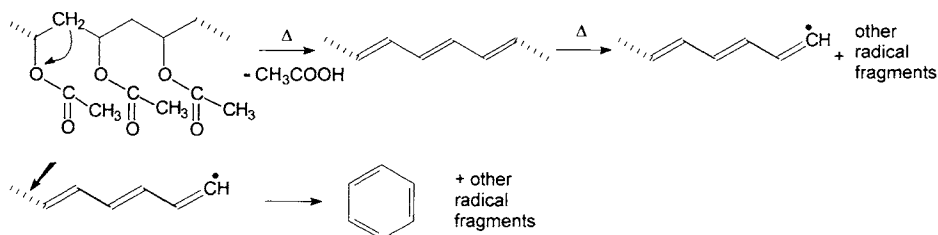
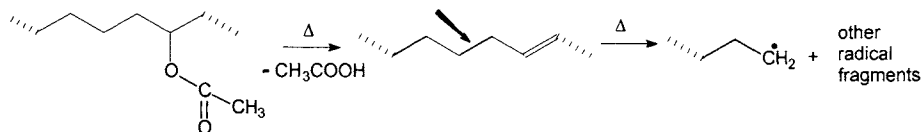


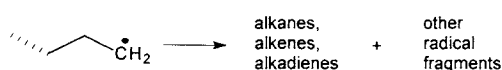
FIGURE 6.1.13. Pyrogram of poly(ethylene-co-vinyl acetate) 9% wt. vinyl acetate. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

Some 2,6-bis(1,1-dimethylethyl)-4-methyl phenol (BHT) which is added as an inhibitor, can be seen in the pyrogram (at 72.20 min.). The difference between the pyrolysis results for the poly(vinyl acetate) homopolymer and that of the copolymer with polyethylene indicates that the acetate groups are sparsely distributed in the copolymer. The differences in the generation of aromatic compounds are indicated schematically below. The poly(vinyl acetate) homopolymer will undergo during pyrolysis reactions of the following type:



On the other hand, for the copolymer the same sequence of reactions does not generate aromatic molecules but similar fragments as obtained from polyethylene:





The presence of larger blocks of vinyl acetate would generate aromatic compounds even for the copolymer, but these were not present in the pyrolysate.

When the proportion of one type of monomeric unit in a copolymer is small, the detection of the presence in the pyrolysis products of that component is sometimes more difficult. As an example, a sample of poly(ethylene-*graft*-maleic anhydride), CAS# 106343-08-2, with 3% wt. maleic anhydride was pyrolyzed at 600° C in He with separation of a Carbowax column. The results are shown in the upper trace in Figure 6.1.14.

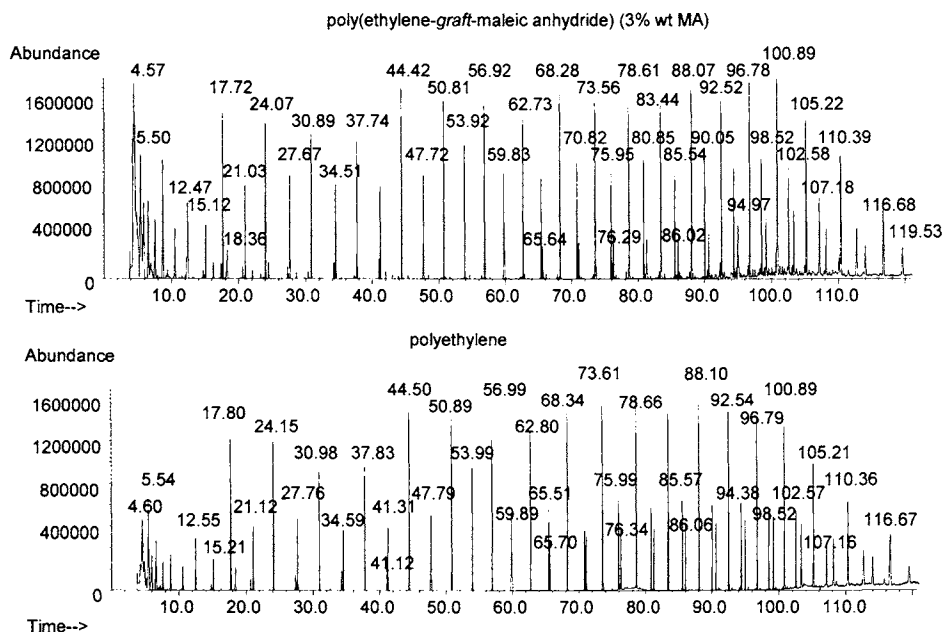


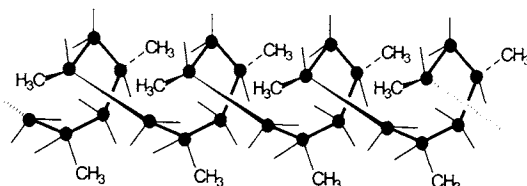
FIGURE 6.1.14. Pyrogram of poly(ethylene-*graft*-maleic anhydride) 3% wt. maleic anhydride (upper trace), and of high-density polyethylene (lower trace). Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

The pyrograms of poly(ethylene-*graft*-maleic anhydride) 3% wt. maleic anhydride and that of high-density polyethylene, shown in the lower trace of Figure 6.1.14, are practically identical. Only the peak corresponding to CO₂ is slightly higher for poly(ethylene-*graft*-maleic anhydride) sample. This is not necessarily a significant finding since variable low levels of CO₂ from traces of air are typically present in pyrograms. The only difference in the two pyrograms is the presence of a few more branched hydrocarbons for the copolymer. These are very similar to those identified in low-density polyethylene. Among the tentatively identified compounds are 3-methyloctene (9.48 min.), 1,2,4-trimethylcyclopentane (12.33 min.), 5-methylenonane (16.27 min.), 3,5,5-trimethyl-1-hexene (17.41 min.), 2-methyl-1-undecene (22.10 min.),

2-propyl-1,1,3-trimethylcyclohexane (24.54 min.), 5-methyl-6-methylenedecane (28.65 min.), etc. The presence of these branched fragment molecules only indicate a branched polymer and cannot be attributed to the elimination during pyrolysis of 2,5-furandione or of dihydro-2,5-furandione or their fragments. Neither 2,5-furandione nor dihydro-2,5-furandione were detected in the pyrogram of poly(ethylene-graft-maleic anhydride). Also, only low traces of compounds such as benzene or toluene were present in the pyrogram.

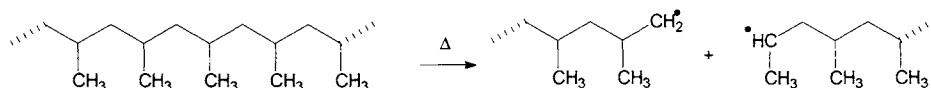
- Polypropylene

Polypropylene (PP) with the formula $[-CH_2CH(CH_3)-]_n$, CAS# 9003-07-0, is a common polymer that is usually obtained by coordination catalyst polymerization. This polymer can be made in isotactic, syndiotactic or atactic forms, typically head to tail. Most practical uses are known for isotactic polypropylene, which is linear and highly crystalline. As indicated in Section 1.3, the linearity of the isotactic polymer implies in fact that the backbone forms a regular spiral that in case of polypropylene has three units per turn, as schematically shown below:

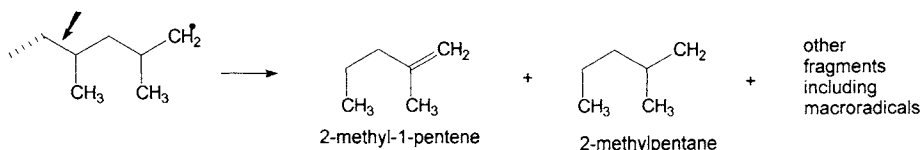


Numerous studies were done for polypropylene pyrolysis [81–98], etc. Also, the kinetics of polypropylene pyrolysis has been studied in detail in an inert atmosphere, in the presence of catalysts or in the presence of other materials such as wood [46, 99–101].

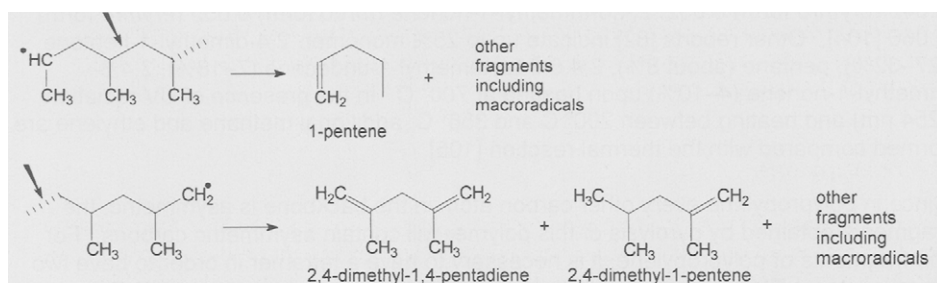
The thermal decomposition of the polymer seems to generate between 10% and 25% propene in addition to other fragments typically with $3n$ number of carbons ($1 \leq n \leq 6$). However, the cleavage of the molecular backbone can take place randomly, and other fragments are generated with $3n+1$ or with $3n-1$ numbers of carbon atoms. The first reaction under the influence of heat is the random scission shown below:



The radicals suffer further reactions with formation of small molecules and other free (macro)radicals. The formation of two small molecules with six carbons (some through hydrogen transfer) are shown below as an example:



Molecules with five or seven carbons are formed through similar reactions, depending on where the radical chain is cleaved, as shown below:



Various published reports show a relatively large variability in the yield of the fragment molecules [102]. The relative amount of fragment molecules depends on the polymer stereoregularity and on the experimental conditions of pyrolysis. The yield of fragments with different numbers of atoms as a function of equilibrium temperature (T_{eq}) is shown for a commercial polypropylene 85% isotactic in Figure 6.1.15 [82].

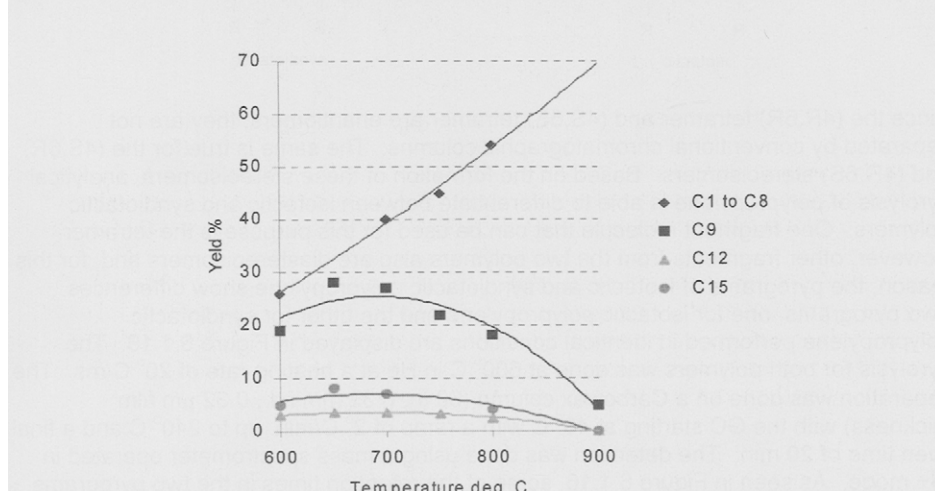
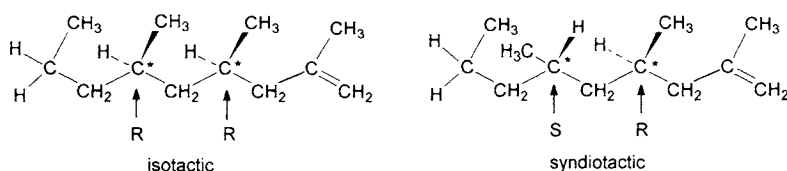


FIGURE 6.1.15. The yield of fragment molecules with a specific number of atoms as a function of equilibrium temperature (T_{eq}) during pyrolysis of polypropylene.

The compounds reported to be obtained from polypropylene during heating [76, 83] include saturated hydrocarbons from C_2 upwards, with monomer yield 0.17% for the heating in the range 328–410° C [55]. The shorter polymer fragments are obtained with higher yield at the expense of larger fragments when temperature increases between 400° C and 1200° C [103]. Heating at 400° C yields chain fragments with 7.05 % wt. of volatile products comprised mainly of methane 0.057 % wt., ethane 0.13, propane 0.078, propene 0.83, isobutene 0.16, butane 0.004, 2-methyl-1-butene 0.010, 1-pentene

0.008, pentane 1.62, 2-pentene (*cis* and *trans*) 0.015, 2-methylpentane 0.074, 2-methyl-1-pentene 1.19, 2,4-dimethylpentane 0.032, 2,4-di-methyl-1-pentene 0.089, 4-methylheptane 0.24, 2,4-dimethyl-1-heptene 2.20, 4,6-dimethylnonane (*threo* form) 0.042 (*erythro* form) 0.052, 2,4,6-trimethyl-1-nonene (*threo* form) 0.055 (*erythro* form) 0.066 [104]. Other reports [82] indicate up to 25% monomer, 2,4-dimethyl-1-heptene (27–32%), pentane (about 8%), 2,4,6,8-tetramethyl-1-undecene (7–18%), 2,4,6-trimethyl-1-nonene (4–10%) upon heating at 700° C. In the presence of UV radiation (254 nm) and heating between 200° C and 356° C, additional methane and ethylene are formed compared with the thermal reaction [105].

Since in polypropylene every other carbon atom in the backbone is asymmetric, the fragments obtained by pyrolysis of this polymer will contain asymmetric carbons. For the fragments of polypropylene, it is necessary to have a tetramer in order to have two chiral centers. These are shown in the following formulas, one containing (R,R) centers, and the other (R,S) centers:



Since the (4R,6R) tetramer and (4S,6S) tetramer are enantiomers, they are not separated by conventional chromatographic columns. The same is true for the (4S,6R) and (4R,6S) stereoisomers. Based on the formation of these stereoisomers, analytical pyrolysis of polypropylene is able to differentiate between isotactic and syndiotactic polymers. One fragment molecule that can be used for this purpose is the tetramer. However, other fragments from the two polymers also are diastereoisomers and, for this reason, the pyrograms of isotactic and syndiotactic polypropylene show differences. Two pyrograms, one for isotactic polypropylene and the other for syndiotactic polypropylene performed in identical conditions are displayed in Figure 6.1.16. The pyrolysis for both polymers was done at 600° C in He at a heating rate of 20° C/ms. The separation was done on a Carbowax column (60 m, 0.32 mm i.d., 0.32 μ m film thickness) with the GC starting at 40° C with a ramp of 2° C/min. up to 240° C and a final oven time of 20 min. The detection was done using a mass spectrometer operated in EI+ mode. As seen in Figure 6.1.16, some of the retention times in the two pyrograms are identical, corresponding to the same compound (with identical chirality or enantiomers). The peaks with different retention times typically indicate different compounds, but some belong to diastereoisomers of the same compound. The peak identification for the chromatograms shown in Figure 6.1.16 was done using MS spectral library searches. These identifications are shown only for the isotactic polymer and are given in Table 6.1.8.

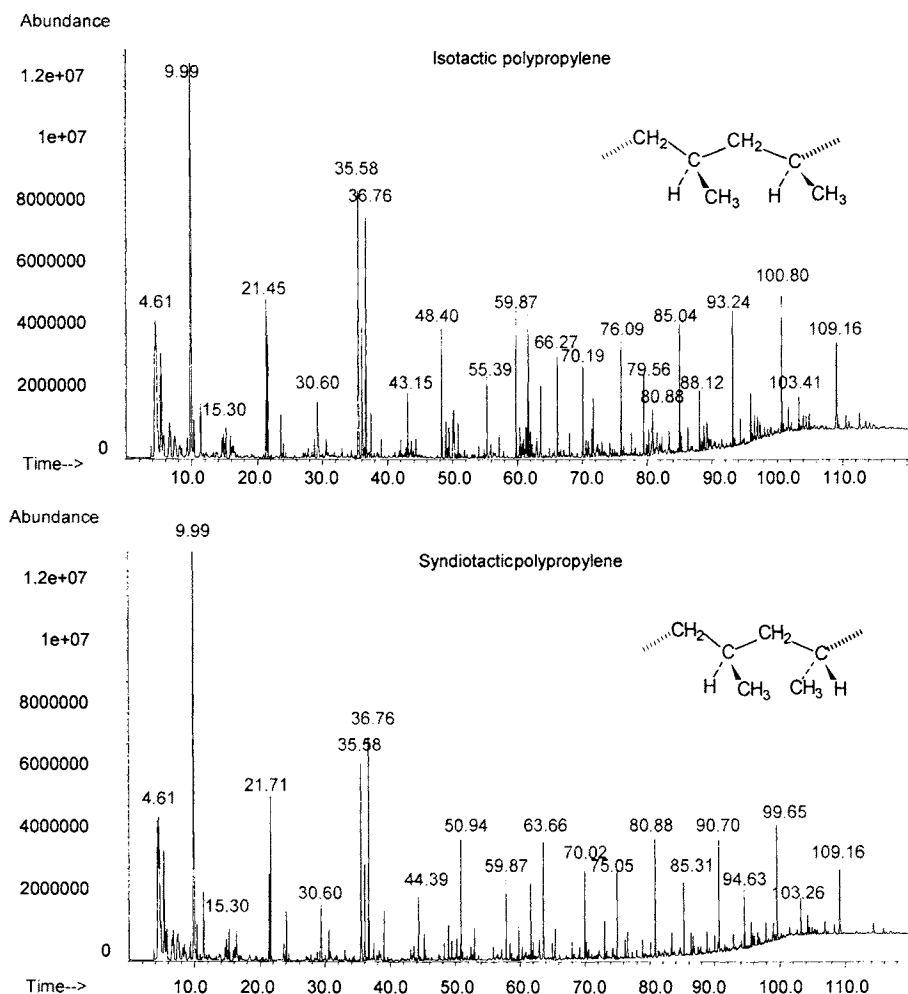


FIGURE 6.1.16. Result for a Py-GC/MS analysis of isotactic polypropylene M_w 12,000 (upper trace) and syndiotactic polypropylene M_w 127,000 (lower trace). Pyrolysis done on 0.4 mg material at 600°C in He, with the separation on a Carbowax type column.

Similar with the case of polyethylene, fragments with higher number of carbons than those shown in the pyrogram from Figure 6.1.16 are generated in the pyrolysates of polypropylene. However, only the compounds with a relatively high volatility can be seen when the GC separation is done on columns that can be heated only up to 240° C (as it is the case for the Carbowax column). The end of the chromatogram for the isotactic polymer shown in Figure 6.1.16 suggests the elution of an additional peak that is interrupted by the end of the chromatographic run.

TABLE 6.1.8. Compounds identified in the pyrogram of isotactic polypropylene as shown in Figure 6.1.16.

Peak	Compound	Ret. Time	MW	Area %
1	propene	4.61	42	6.32
2	2-methyl-1-propene	4.66	56	1.66
3	2-methylbutane	4.70	72	1.33
4	1-pentene	4.80	70	trace
5	2-methylpentane (dimer of propene)	4.92	86	0.33
6	2-methyl-1-pentene	5.33	84	4.07
7	2,4-dimethyl-1-pentene	5.80	98	0.67
8	2,4-dimethyl-1,4-pentadiene	6.58	96	trace
9	4-methylheptane	6.73	114	1.67
10	4-methyl-2-heptene	7.45	112	1.08
11	1,3,5-trimethylcyclohexane	9.34	126	0.59
12	2,4-dimethyl-1-heptene (trimer of propene)	9.99	126	14.68
13	1,2,4-trimethylcyclohexane (1.alpha.,2.beta.,4.beta.)	10.41	126	0.91
14	2,4,6-trimethyl-1-heptene	11.42	140	1.08
15	2,6-dimethylnonane	14.70	156	0.53
16	4-methyldecane	14.89	156	0.56
17	2,4,6-trimethyl-1-octene	15.30	154	0.45
18	2,4,6-trimethyl-1-octene diastereoisomer	15.97	154	0.25
19	2,4,6-trimethyl-1-nonene	21.45	168	2.98
20	2,4,6-trimethyl-1-nonene diastereoisomer	21.70	168	2.02
21	2,4,6,8-tetramethyl-1-nonene	23.67	182	0.60
22	dimethylundecene ?	24.09	182	0.24
23	C14;1	28.83	196	0.39
24	unknown	29.30		1.08
25	C14;1	30.60	196	0.47
26	unknown	33.05		0.33
27	2,4,6,8-tetramethyl-1-undecene (C15;1)	35.58	210	5.77
28	2,4,6,8-tetramethyl-1-undecene (C15;1) diastereoisomer	36.15	210	2.89
29	2,4,6,8-tetramethyl-1-undecene (C15;1) diastereoisomer	36.76	210	4.64
30	C16;1	37.48	224	0.79
31	unknown	39.08		0.28
32	C17;1	42.07	238	0.23
33	C16;2	43.15	222	0.95
34	unknown	43.67		0.40
35	unknown	44.38		0.26
36	C18;1	48.40	252	0.98
37	C18;1 diastereoisomer	48.96	252	1.00
38	C18;1 diastereoisomer	49.06	252	0.93
39	C18;1 diastereoisomer	49.50	252	0.66
40	C18;1 diastereoisomer	50.10	252	trace
41	C18;1 diastereoisomer	50.24	252	1.85
42	C18;1 diastereoisomer	50.34	252	trace
43	C18;1 diastereoisomer	50.92	252	0.53
44	C19;2	55.39	264	1.15
45	C19;2	57.22	264	0.35
46	C21;1	59.88	294	2.46
47	unknown	60.45		0.66
48	unknown	61.00		0.74
49	unknown	61.41		0.68
50	C21;1 diastereoisomer	61.73	294	2.69
51	unknown	62.08		0.46

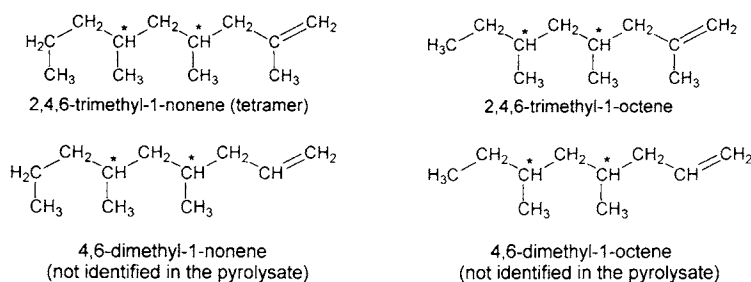
TABLE 6.1.8 (continued). Compounds identified in the pyrogram of isotactic polypropylene as shown in Figure 6.1.16.

Peak	Compound	Ret. Time	MW	Area %
52	unknown	62.34		0.25
53	unknown	63.05		0.67
54	C21;1 diastereoisomer	63.66	294	1.25
55	C22;2	66.27	306	1.31
56	C22;2	68.07	306	0.30
57	C24;1	70.19	336	1.44
58	unknown	71.77		0.96
59	C25;2	76.09	348	1.49
60	C25;2	77.63	348	0.35
61	C27;1	79.56	378	1.17
62	unknown	79.96		1.52
63	unknown	83.44		0.76
64	C28;2	85.04	390	1.64
65	C26;1 ?	88.12	364	0.93
66	unknown	89.27		0.75
67	C31;2	93.24	432	1.86
68	C31;2	94.39	432	0.37
69	C29;1	96.00	406	0.82
70	unknown	96.63		0.52
71	unknown	97.04		0.65
72	C34;2	100.80	474	1.96
73	unknown	103.41		0.78
74	C37;2	109.16	516	1.88
75	C37;2	110.58	516	0.31
76	unknown	112.70		0.43

Many compounds in the pyrogram were identified only as hydrocarbon with a specific number of carbon atoms and double bonds. The use of mass spectral library search was not always sufficient for the complete compound identification.

Similar to polyethylene, the presence of a large number of peaks with relatively equal intensity in the pyrogram suggests that the pyrolysis mechanism starts with a random scission. The presence of alkanes, alkenes, and dienes shows that this process is terminated by disproportionation. The peak with relatively higher intensity is the propylene trimer (2,4-dimethyl-1-heptene), probably the most stable compound in the pyrolysis conditions used for this particular experiment.

Additional complexity in the chromatograms of either isotactic or syndiotactic polypropylene is brought by the fact that the polymers may have some steric irregularities [106]. Also, the chirality of the fragments may be affected during pyrolysis, depending on the stability of the molecular fragments formed from the polymer and the decomposition mechanism during pyrolysis [107]. This leads to the formation of various diastereoisomers regardless which stereoregular polymer is pyrolyzed. Examples of compounds that potentially can be found in polypropylene pyrolysate and generate diastereoisomers from two asymmetric carbons are shown below:



The (4*R*,6*R*) diastereoisomer (and/or (4*S*,6*S*)) will be proportionally at a higher level in the pyrolysate of the isotactic polymer, while the (4*R*,6*S*) (and/or (4*S*,6*R*)) will be higher in the pyrolysate of the syndiotactic polymer. This is shown in Figure 6.1.17 for the case of 2,4,6-trimethyl-1-nonene (propylene tetramer), which gives two peaks in the pyrogram, one at 21.45 min. and the other at 21.70 min. (see also Figure 6.1.16).

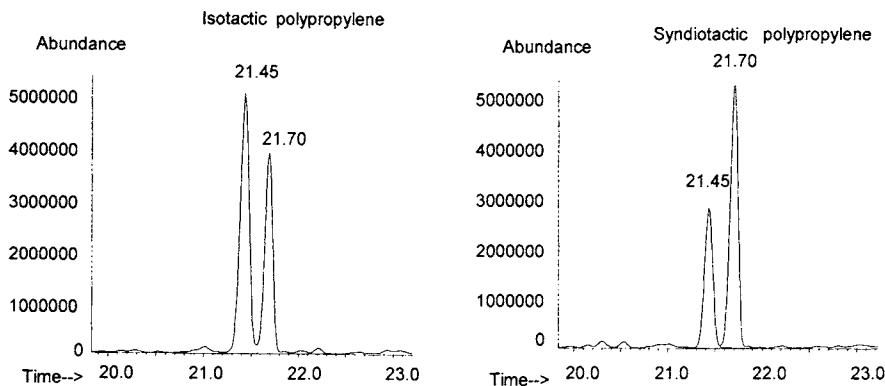


FIGURE 6.1.17. Two peaks at 21.45 min. and 21.70 min. corresponding to the two diastereoisomers of 2,4,6-trimethyl-1-nonene obtained by Py-GC/MS from syndiotactic and isotactic polypropylene, respectively. (The time windows 20 min. to 23 min. are obtained from the pyrograms shown in Figure 6.1.16.)

The spectra of the two diastereoisomers identified as 2,4,6-trimethyl-1-nonene are practically identical, as shown in Figure 6.1.18.

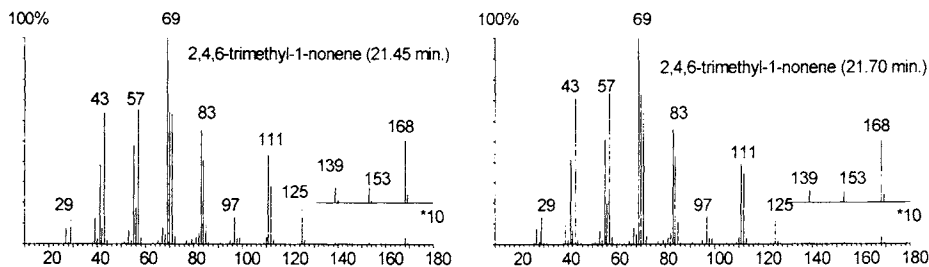


FIGURE 6.1.18. Mass spectra of the two diastereoisomers of 2,4,6-trimethyl-1-nonene (MW = 168).

The number of possible stereoisomers (with ends that are not identical) is given by 2^n where n is the number of chiral centers in the molecule. The number of enantiomers and that of diastereoisomers is 2^{n-1} . For example, the pentamer has three chiral centers and therefore four diastereoisomers. Only three different peaks eluting at 35.58 min., 36.15 min. and 36.76 min. correspond to the four pentamer stereoisomers, two of the diastereoisomers eluting very likely together. The spectra for the pentamers are shown in Figure 6.1.19.

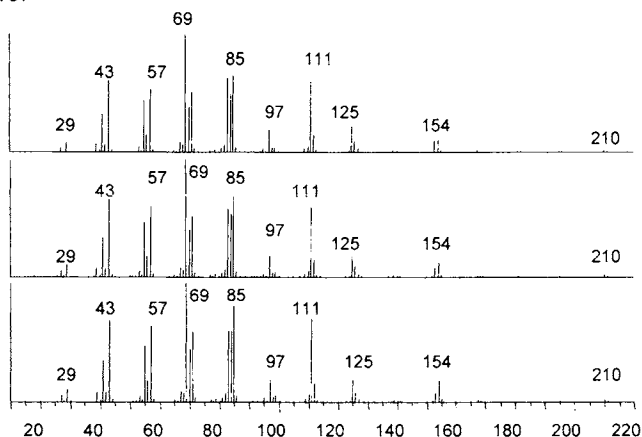


FIGURE 6.1.19. Mass spectra of several diastereoisomers of 2,4,6,8-tetramethyl-1-undecene, propylene pentamer (MW = 210) eluting at 35.58 min., 36.15 min. and 36.76 min. in the pyrogram shown in Figure 6.1.17.

The next set of diastereoisomers corresponds to the hexamer of propylene, which has four chiral centers and generates eight diastereoisomers. The eight peaks corresponding to these compounds can be seen in the pyrograms shown in Figure 6.1.16, and they elute between 48.0 min. and 52.0 min. This time window of the pyrogram for the isotactic and syndiotactic polypropylene has been shown enlarged in Section 4.3 (see Figure 4.3.1). The peak eluting at 48.40 min. and assigned to (R,R,R,R) diastereoisomer is significantly higher in the pyrolysate of isotactic polypropylene, while the peak assigned to (R,S,R,S) diastereoisomer is higher in syndiotactic pyrolysate. The mass spectra of all these diastereoisomers are practically identical, as expected. The mass spectrum of the peak eluting at 48.40 min. is shown in Figure 6.1.20.

Other oligomers in the chromatograms show similar behavior regarding the intensity of diastereoisomers peaks. However, the assignment of the chemical nature of higher molecular weight compounds is more difficult.

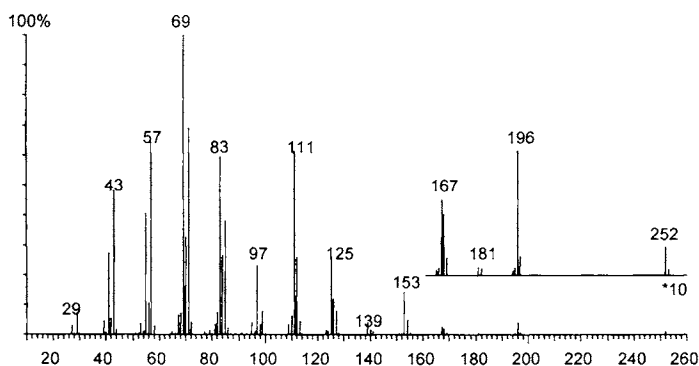


FIGURE 6.1.20. Mass spectrum of 2,4,6,8,10-pentamethyl-1-tridecene, propylene hexamer ($C_{18};1$) ($MW = 252$).

Pyrolysis of amorphous polypropylene (with unspecified stereoregularity and M_w 14,000) in identical conditions as those for the stereoregular polymers leads to a pyrogram shown in Figure 6.1.21.

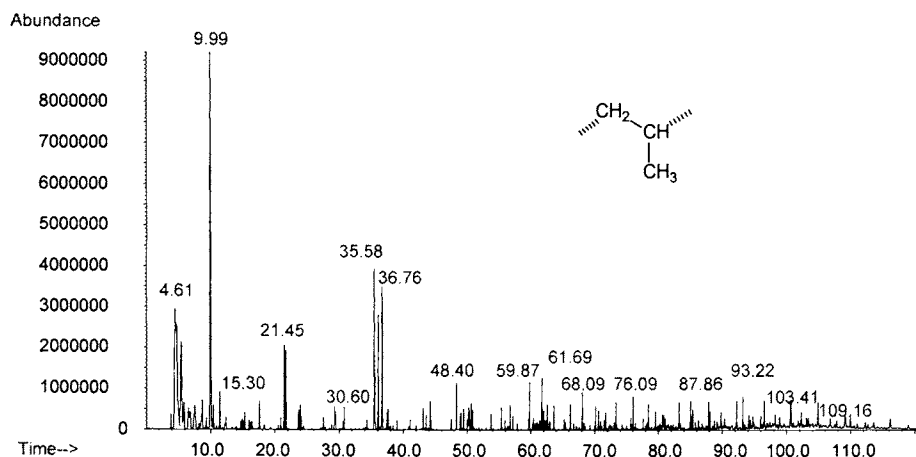


FIGURE 6.1.21. Result for a Py-GC/MS analysis of amorphous polypropylene M_w 14,000. Pyrolysis done on 0.4 mg material at $600^\circ C$ in He, with the separation on a Carbowax type column.

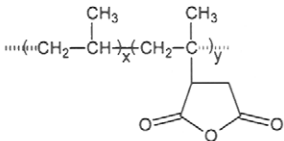
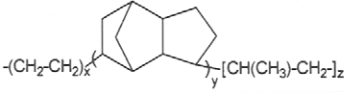
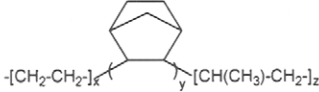
Most peaks in the pyrogram shown in Figure 6.1.21 are identified in Table 6.1.8, being identical to those for stereoregular polymers. However, the peak intensities can be significantly different for different polymers, depending on stereoregularity. A systematic study of the peak intensity of different diastereoisomers allows the estimation of stereospecific type of polypropylene, and even that of the average sequence length of syndiotactic sequence and of the isotactic sequence in a polymer [61].

The results of pyrolysis of polypropylene in air depends on the pyrolysis heating rate because the pyrolysis process competes with the oxidation [108]. By heating between 120° C and 280° C in air, polypropylene is reported to generate ethene, ethane, propene, propane, isobutene, butane, isobutane, pentadiene, 2-methyl-1-pentene, 2,4-dimethyl-1-pentene, 5-methyl-1-heptene, dimethylbenzene, methanol, ethanol, 2-methyl-2-propene-1-ol, 2-methylfuran, 2,5-dimethylfuran, formaldehyde, acetaldehyde, acrolein, propanal, methacrolein, 2-methylpropanal, butanal, 2-vinylcrotonaldehyde, 3-methylpentanal, 3-methylhexanal, octanal, nonanal, decanal, ethenone, acetone, 3-buten-2-one, 2-butanone, 1-hydroxy-2-propanone, 1-cyclopropylethanone, 3-methyl-2-buten-2-one, 3-penten-2-one, 2-pentanone, 2,3-butanedione [109].

- Copolymers of propylene

Similar to ethylene, propylene is used in a considerable number of copolymers. Some common copolymers of propylene are indicated in Table 6.1.9.

TABLE 6.1.9. Common copolymers of propylene

Copolymer name	CAS #	Structure
poly(1-propene- <i>alt</i> -ethene)	127883-08-3	$[-CH(CH_3)-CH_2-CH_2-CH_2-]_n$
poly(1-propene- <i>block</i> -ethene)	106565-43-9	$[-CH(CH_3)-CH_2]_x[-CH_2-CH_2-]_y$
poly(1-propene-co-1-butene)	29160-13-2	$[-CH(CH_3)-CH_2]_x[-CH(CH_2CH_3)-CH_2]_y$
poly(1-propene-co-ethene)	9010-79-1	$[-CH(CH_3)-CH_2]_x[-CH_2-CH_2-]_y$
poly(1-propene-co-SO ₂)	30475-44-6	$[-CH(CH_3)-CH_2]_x[-SO_2-]_y$
poly(chloroethene-co-1-propene)	72027-02-2	$[-CH(CH_3)-CH_2]_x[-CH(Cl)-CH_2]_y$
poly(tetrafluoroethene-co-1-propene)	27029-05-6	$[-CH(CH_3)-CH_2]_x[-CF_2CF_2-]_y$
polypropylene-graft-maleic anhydride	107001-49-0	
poly(ethene- <i>alt</i> -1-propene- <i>alt</i> -SO ₂)	122752-93-6	$[-CH_2-CH_2-SO_2-CH(CH_3)-CH_2]_x$
poly(propylene- <i>alt</i> -carbon monoxide- <i>alt</i> -ethylene)	121520-83-0	$[-CH_2-CH_2-CO-CH(CH_3)-CH_2]_x$
poly(dicyclopentadiene-co-ethylene-co-propene) rubber		
poly(ethylene-co-ethylidenenorbornene-co-propene) rubber		
poly(ethylene-co-propylene-co-diene) rubber		$[-CH(CH_3)-CH_2]_x[-CH_2(CH)_2CH_2-]_y$
poly(ethylene-co-hexadiene-co-propene) rubber		$[-CH(CH_3)-CH_2]_x[-CH_2(CH)_4CH_2-]_y$
poly(propylene-co-carbon monoxide-co-ethylene)	88995-51-1	$[-CH(CH_3)-CH_2]_x[-CO-]_y[-CH_2-CH_2-]_z$

Polypropylene is also used in a number of blends, some of them with applications in rubber industry, automotive industry, home constructions, etc. Some of the copolymers and blends used in rubber industry are vulcanized. Studies on thermal properties and pyrolysis of these copolymers and blends are common in literature [97, 105, 110–118].

Two examples of propylene copolymers pyrolysis are given below. The first example is for poly(propylene-co-1-butene) 14 % wt. butene, CAS# 29160-13-2. The pyrogram is shown in Figure 6.1.22. The pyrolysis was done at 600° C in He with separation on a Carbowax column and MS detection, similarly to other polymers previously discussed in this book (see also Table 4.2.2).

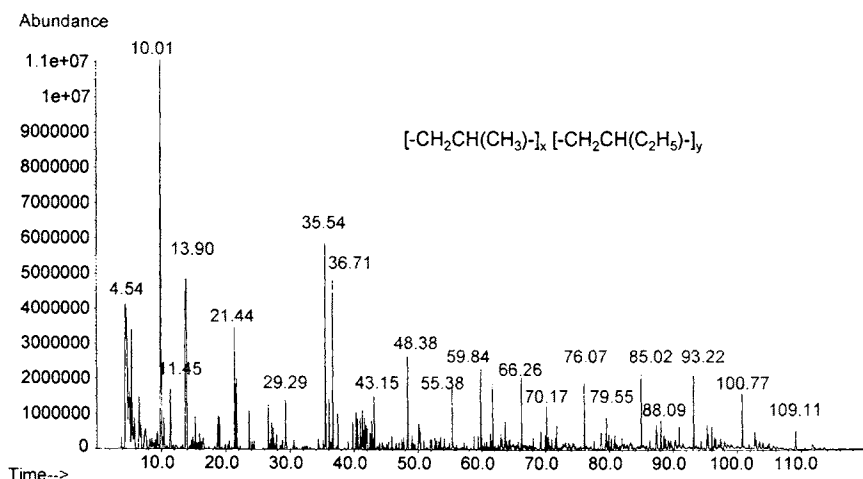


FIGURE 6.1.22. Pyrogram of poly(propylene-co-1-butene) 14 % wt. butene. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

The pyrogram is rather complex and suggests that the copolymer has a random structure. Fragments originating from polypropylene with structures of the type AA, AAA, AAAA, etc., fragments from poly(1-butene) of the type BB, BBB, BBBB, as well as fragments of the type AB, AAB, ABB, etc. are present in the pyrogram. However, since the molar ratio of the two monomers propene/1-butene is approximately 8/1, the dominant peaks are similar to those generated from polypropylene. Peak identification is complicated also because various types of fragments are generated by the cleavage of the C–C bonds, which have very similar bond energy in the whole polymer. Also, both polymers have asymmetric carbons for each monomer. This leads to the formation of numerous peaks with the same spectrum. A time window between 40.0 min. and 54.0 min. from Figure 6.1.22 is expanded and is shown in Figure 6.1.23. The spectra of the first 10 peaks shown in Figure 6.1.23 are similar and contain a molecular ion corresponding to MW = 224. Several further peaks correspond to MW = 238.

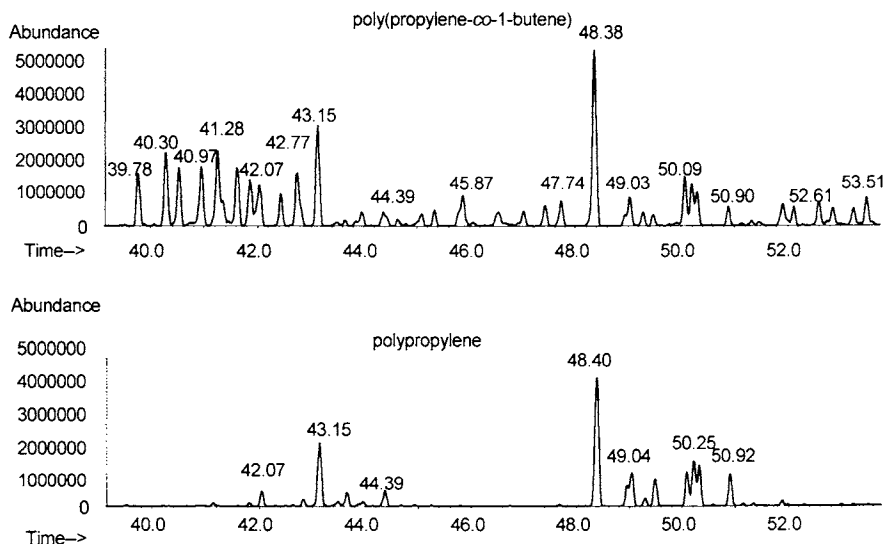
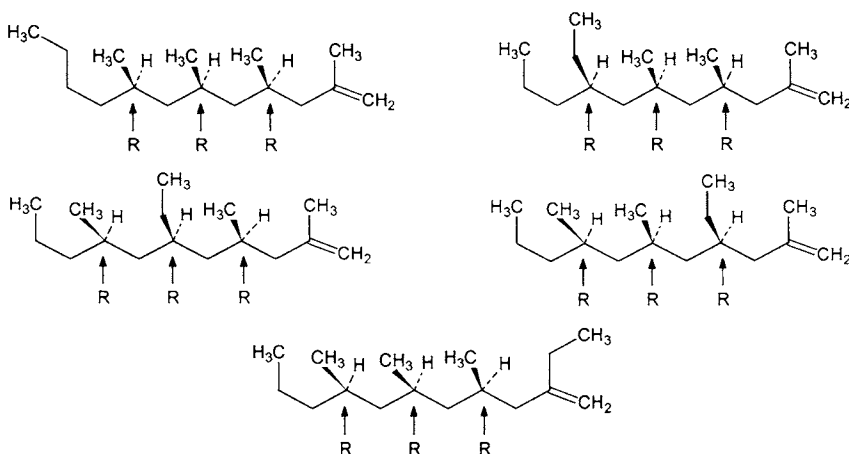


FIGURE 6.1.23. Time window 40.0 min to 54.0 min from the pyrogram of poly(propylene-co-1-butene) 14 wt % butene. Whole pyrogram shown in Figure 6.1.22.

The peaks showing the molecular ion $m/z = 224$ have the molecular formula $C_{16}H_{32}$. A number of molecules with this formula can be generated, some from the cleavage of bonds within the monomeric units, and some with the cleavage between the monomeric units of the polymer. The fragments generated such that the monomeric units are preserved should have the formula $(C_3H_7)_4C_4H_8$. Using only this model with intact monomeric units, several structures are possible as indicated below:



Each of the previous structures contains three chiral centers and will generate four diastereoisomers. Adding other models that correspond to fragment molecules

generated from the cleavage of bonds within the monomeric units, the number of possibilities is even higher. Although precise assignments for the peaks were not possible, this variety of compounds easily explains the formation of numerous peaks with identical or very similar mass spectra in the copolymer pyrogram.

One other example of a pyrogram of a copolymer is that for poly(propylene-*graft*-maleic anhydride) or polypropylene-*graft*-poly[3-(1-methyl-1-propenyl)-3,4-dihydrofuran-2,5-dione, CAS# 107001-49-0. The polypropylene polymer was isotactic and had a low content of maleic anhydride (MA) and a $M_w = 9,100$. The pyrolysis was performed in conditions similar to other examples, at 600° C in He with separation of a Carbowax column. The results are shown in Figure 6.1.24.

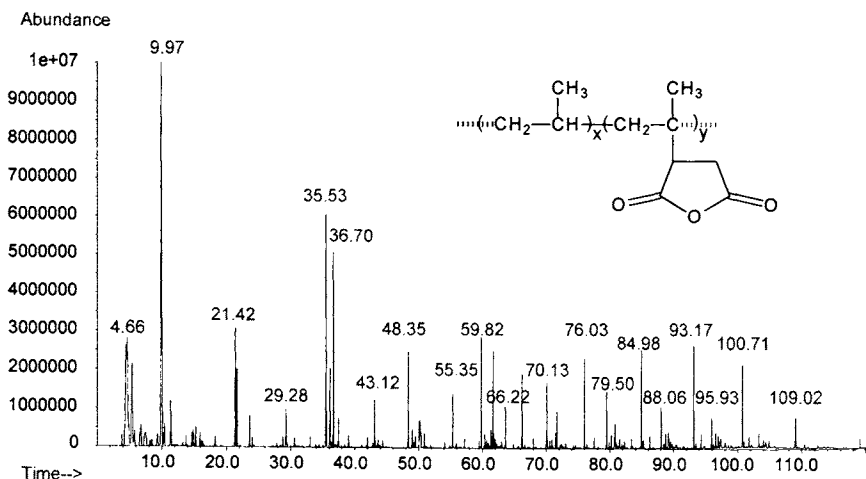


FIGURE 6.1.24. Pyrogram of poly(propylene- *graft*-maleic anhydride) (low content of MA). Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

The pyrogram of this copolymer is almost identical to that of isotactic polypropylene, and no trace of the graft units were seen in the pyrolysate. The same results were obtained for the pyrolysis of poly(ethylene-*graft*-maleic anhydride) 3% wt. maleic anhydride (see Figure 6.1.14). The graft units cannot be detected for this polymer, using Py-GC/MS.

- Polyisobutene

Polyisobutene or polyisobutylene, CAS# 9003-27-4, with the model formula $[-\text{CH}_2\text{C}(\text{CH}_3)_2-]_n$ is another common polymer, which is used in practice mainly for sealants and adhesives and in various copolymers. Polyisobutylene copolymer with a small amount of isoprene is used as a synthetic rubber, the added isoprene making the material vulcanizable. The polymer is typically obtained by cationic polymerization using, for example, BF_3 or AlCl_3 as catalysts. The thermal decomposition of the polymer generates various fragments [76, 119–123]. The heating between 288° C and 425° C

generates 18.1% monomer together with methane, isobutane, and C_5 and higher saturated and unsaturated hydrocarbons [56]. The heating up to 1200°C forms fragments, and as the temperature increases, the fragments even smaller than the monomer have a yield increase at the expense of larger fragments [103]. The heating at 325°C is reported to produce, at 4.9% weight loss, isobutene (64.3%), methane (13.6%), neopentane (10.3%) and a remainder of C_2 - C_{12} hydrocarbons [122]. Heating at 345°C gives a 15.7% weight loss and produces isobutene (78.9%), methane (5.9%), neopentane (4.7%) and a remainder of C_2 - C_{12} hydrocarbons. Heating at 365°C produces a 46.8% weight loss and isobutene (81.6%), methane (3.9%), neopentane (3.1%), and a remainder of C_2 - C_{12} hydrocarbons. The heating between 300°C and 320°C is reported to form two types of *tert*-butyl ended and two types of isopropyl ended monoolefins in the range of 2 to 12 monomer units [124].

The results for a Py-GC/MS analysis of a polyisobutene sample are shown in Figure 6.1.25. The pyrolysis was done at 600°C in He at a heating rate of 20°C/ms . The separation was done on a Carbowax column (60 m, 0.32 mm i.d., 0.32 μm film thickness) with the GC starting at 40°C with a ramp of 2°C/min . up to 240°C and a final oven time of 20 min. The MS was operated in EI+ mode.

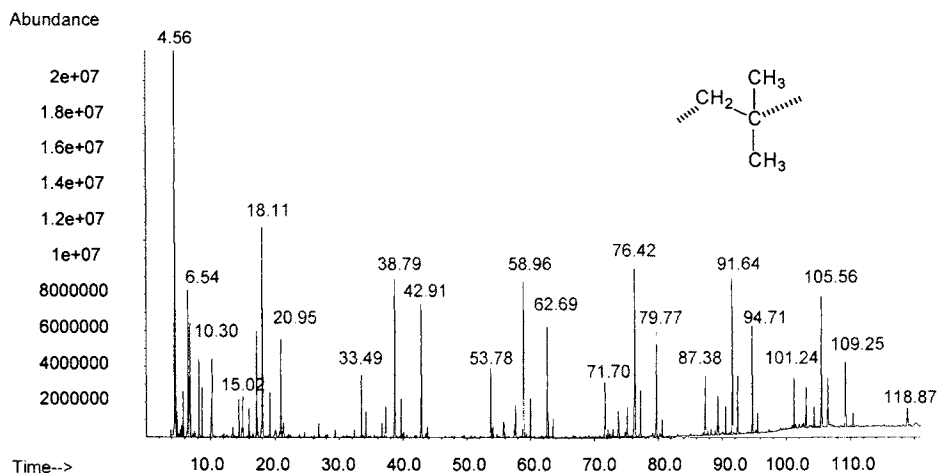
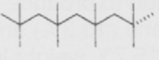

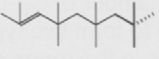

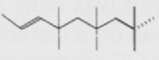





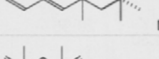

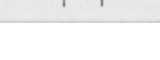


FIGURE 6.1.25. Result for a Py-GC/MS analysis of polyisobutene with M_w 420,000. Pyrolysis done on 0.4 mg material at 600°C in He, with the separation on a Carbowax type column.

Table 6.1.10 shows the main types of fragments generated during pyrolysis of polyisobutylene. The group $-\text{CH}_2-\text{C}(\text{CH}_3)_2-$ is repeated "n" times in various fragments. The type of fragment is indicated in the table by the letters A, B, C,..., and the number of repetitions of the group $-\text{CH}_2-\text{C}(\text{CH}_3)_2-$ is given by the index n.

TABLE 6.1.10. *Main types of fragment molecules generated by pyrolysis of polyisobutene.*

Type	Formula	Structure
An	$\text{H}[-\text{CH}_2-\text{C}(\text{CH}_3)_2]_n-\text{CH}_3$	 n=4
B0	$(\text{CH}_3)_2\text{C}=\text{CH}-\text{C}(\text{CH}_3)_2-\text{CH}_3$	 n=0
Bn	$(\text{CH}_3)_2\text{C}=\text{CH}-\text{C}(\text{CH}_3)_2-[\text{CH}_2-\text{C}(\text{CH}_3)_2]_n-\text{CH}_3$	 n=2
C0	$\text{CH}_3-\text{CH}=\text{CH}-\text{C}(\text{CH}_3)_2-\text{CH}_3$	 n=0
Cn	$\text{CH}_3-\text{CH}=\text{CH}-\text{C}(\text{CH}_3)_2-[\text{CH}_2-\text{C}(\text{CH}_3)_2]_n-\text{CH}_3$	 n=2
D0	$\text{CH}_2=\text{C}(\text{CH}_3)_2$	 n=0
Dn	$\text{CH}_2=\text{C}(\text{CH}_3)-[\text{CH}_2-\text{C}(\text{CH}_3)_2]_n-\text{CH}_3$	 n=3
E0	$\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{C}(\text{CH}_3)-\text{CH}_3$	 n=0
En	$\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{C}(\text{CH}_3)-[\text{CH}_2-\text{C}(\text{CH}_3)_2]_n-\text{CH}_3$	 n=2
F0	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{C}(\text{CH}_3)_2-\text{CH}_3$	 n=0
Fn	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{C}(\text{CH}_3)_2-[\text{CH}_2-\text{C}(\text{CH}_3)_2]_n-\text{CH}_3$	 n=1
G0	$\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}_2-\text{C}(\text{CH}_3)=\text{CH}_2$	 n=0
Gn	$\text{CH}_2=\text{C}(\text{CH}_3)-[\text{CH}_2-\text{C}(\text{CH}_3)_2]_n-\text{CH}_2-\text{C}(\text{CH}_3)=\text{CH}_2$	 n=2

The peak identification for the chromatogram shown in Figure 6.1.25 was done using MS spectral library searches. This identification is not always possible, since most compounds with a higher MW are not found in the commercial mass spectral libraries (such as NIST 2002, Wiley 7, etc.). The similarity between the spectra in each series of compounds can be used for peak identification, even when the compound is not found in the mass spectral library. This is exemplified in Figure 6.1.26, which shows the spectra of the B series of compounds shown in Table 6.1.10.

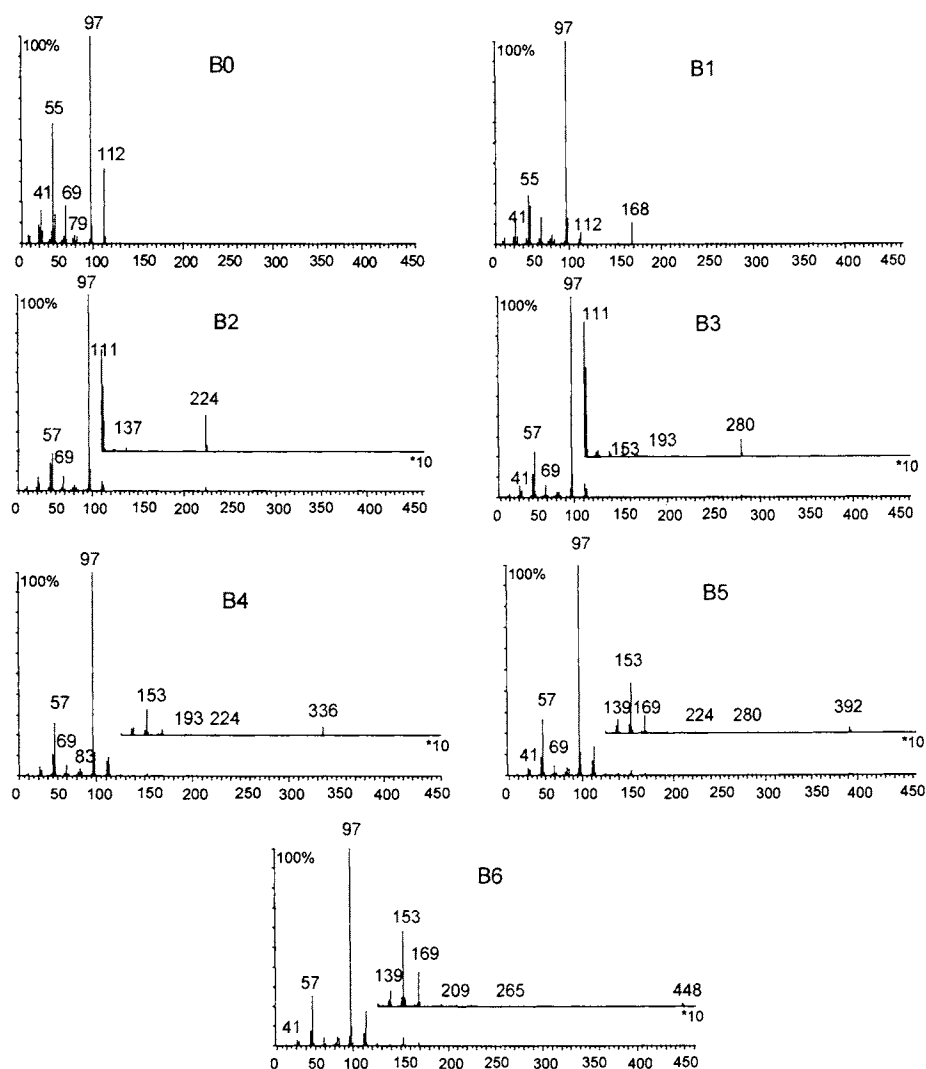


FIGURE 6.1.26. Spectra of the series B_n of compounds indicated in Table 6.1.10 and found in the pyrogram of poly(isobutylene); $M_w(B0) = 112$, $M_w(B1) = 168$, $M_w(B2) = 224$, $M_w(B3) = 280$, $M_w(B4) = 336$, $M_w(B5) = 392$, $M_w(B6) = 448$.

The list of peak identifications for the pyrogram shown in Figure 6.1.25 is given in Table 6.1.11.

TABLE 6.1.11. Compounds identified in the pyrogram of polyisobutene as shown in Figure 6.1.25.

Peak	Type	Compound	Ret. Time	Mass	Area%
1	A1	2,2-dimethylpropane	4.46	72	2.11
2	D0	2-methylpropene	4.56	56	8.72
3		2-methyl-1-butene	4.86	70	0.40
4		2,2,4-trimethylpentane	5.55	114	0.20
5	C0	4,4-dimethyl-2-pentene	5.79	98	0.83
6	D1	2,4,4-trimethyl-1-pentene	6.54	112	3.24
7	A2	2,2,4,4-tetramethylpentane	6.73	128	1.10
8	B0	2,4,4-trimethyl-2-pentene	6.86	112	2.27
9	E0	2,4-dimethyl-1,3-pentadiene	8.25	96	1.34
10		3,5,5-trimethyl-1-hexene	8.70	126	0.95
11		2,4-dimethyl-1,5-hexadiene	10.17	110	0.68
12	F0	5,5-dimethyl-1,3-hexadiene	10.30	110	1.46
13	G0	2,4-dimethyl-2,4-pentadiene	11.76	96	trace
14		1,1,3,3,5-pentamethylcyclohexane	13.50	154	0.28
15	C1	4,4,6,6-tetramethyl-2-heptene	14.43	154	0.85
16	E1	2,4,7,7-tetramethyl-1,3-heptadiene	14.87	152	0.17
17	D2	2,4,4,6,6-pentamethyl-1-heptene	15.02	168	0.91
18		5-methyldecene?	15.99	154	0.70
19	F1	5,5,7,7-tetramethyl-1,3-octadiene	17.20	166	2.14
20		a pentamethylheptene	17.83	168	0.19
21	B1	2,4,4,6,6-pentamethyl-2-heptene	18.11	168	6.58
22	G1	2,4,4,6-tetramethyl-1,6-heptadiene	19.23	152	0.96
23	A3	2,2,4,4,6,6-hexamethylheptane	20.95	184	2.29
24	E2	2,4,7,7,9,9-hexamethyl-1,3-nonadiene	21.35	208	0.50
25		a hexamethylheptene	26.87	182	0.28
26		a hexamethylnonene	29.43	210	0.23
27	C2	4,4,6,6,8,8-hexamethyl-2-nonene	33.49	210	1.39
28	D3	2,4,4,6,6,8,8-heptamethyl-1-nonene	34.18	224	0.57
29		a heptamethylnonene	36.73	224	0.30
30	F2	5,5,7,7,9,9-hexamethyl-1,3-decadiene ?	37.30	222	0.76
31	B2	2,4,4,6,6,8,8-heptamethyl-2-nonene	38.79	224	4.75
32	G2	2,4,4,6,6,8-hexamethyl-1,6-nonadiene	39.71	208	0.81
33	A4	2,2,4,4,6,6,8,8-octamethylnonane	42.91	240	3.50
34	E3	2,4,7,7,9,9,11,11-octamethyl-1,3-undecadiene	43.84	264	0.22
35	C3	4,4,6,6,8,8,10,10-octamethyl-2-undecene	53.78	266	1.59
36		a hexamethyldecadiene ?	54.13	222	0.23
37	D4	2,4,4,6,6,8,8,10,10-nonamethyl-1-undecene	55.77	280	0.36
38		a nonamethylundecene	55.88	280	0.29
39	F3	5,5,7,7,9,9,11,11-octamethyl-1,3-dodecadiene	57.65	278	0.71
40	B3	2,4,4,6,6,8,8,10,10-nonamethyl-2-undecene	58.96	280	5.16
41	G3	2,4,4,6,6,8,8,10-octamethyl-1,6-undecadiene	60.00	264	0.82
42	A5	2,2,4,4,6,6,8,8,10,10-decamethylundecane	62.69	296	2.79
43	E4	2,4,7,7,9,9,11,11,13,13-decamethyl-1,3-tridecadiene	63.55	320	0.42
44	C4	4,4,6,6,8,8,10,10,12,12-undecamethyl-2-tridecene	71.70	322	1.53
45	D5	2,4,4,6,6,8,8,10,10,12,12-undecamethyl-1-tridecene	73.80	336	0.90
46	F4	5,5,7,7,9,9,11,11,13,13-decamethyl-1,3-tetradecadiene	75.18	334	0.72
47	B4	2,4,4,6,6,8,8,10,10,12,12-undecamethyl-2-tridecene	76.42	336	5.55
48	G4	2,4,4,6,6,8,8,10,10,12-octamethyl-1,6-undecadiene	77.25	320	1.10
49	A6	2,2,4,4,6,6,8,8,10,10,12,12-dodecamethyltridecane	79.77	352	2.74
50	E5	$\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{C}(\text{CH}_3)-[\text{CH}_2-\text{C}(\text{CH}_3)_2]_5\text{CH}_3$	80.64	376	0.40

TABLE 6.1.11 (continued). Compounds identified in the pyrogram of polyisobutene as shown in Figure 6.1.25.

Peak	Type	Compound	Ret. Time	Mass	Area%
51	C5	$\text{CH}_3\text{-CH=CH-C(CH}_3)_2\text{-[CH}_2\text{-C(CH}_3)_2\text{]}_5\text{-CH}_3$	87.38	378	1.33
52	D6	$\text{CH}_2\text{=C(CH}_3\text{)-[CH}_2\text{-C(CH}_3)_2\text{]}_6\text{-CH}_3$	89.35	392	0.92
53	F5	$\text{CH}_2\text{=CH-CH=CH-C(CH}_3)_2\text{-[CH}_2\text{-C(CH}_3)_2\text{]}_5\text{-CH}_3$	90.53	390	0.59
54	B5	$\text{(CH}_3)_2\text{C=CH-C(CH}_3)_2\text{-[CH}_2\text{-C(CH}_3)_2\text{]}_5\text{-CH}_3$	91.64	392	4.30
55	G5	$\text{CH}_2\text{=C(CH}_3\text{)-[CH}_2\text{-C(CH}_3)_2\text{]}_5\text{-CH}_2\text{C(CH}_3\text{)=CH}_2$	92.43	376	1.31
56	A7	$\text{H-[CH}_2\text{-C(CH}_3)_2\text{]}_7\text{-CH}_3$	94.71	408	2.58
57	E6	$\text{CH}_2\text{=C(CH}_3\text{)-CH=C(CH}_3\text{)-[CH}_2\text{-C(CH}_3)_2\text{]}_6\text{CH}_3$	95.54	432	0.43
58	C6	$\text{CH}_3\text{-CH=CH-C(CH}_3)_2\text{-[CH}_2\text{-C(CH}_3)_2\text{]}_6\text{-CH}_3$	101.24	434	1.17
59	D7	$\text{CH}_2\text{=C(CH}_3\text{)-[CH}_2\text{-C(CH}_3)_2\text{]}_7\text{-CH}_3$	103.12	448	1.08
60	F6	$\text{CH}_2\text{=CH-CH=CH-C(CH}_3)_2\text{-[CH}_2\text{-C(CH}_3)_2\text{]}_6\text{-CH}_3$	104.36	446	0.54
61	B6	$\text{(CH}_3)_2\text{C=CH-C(CH}_3)_2\text{-[CH}_2\text{-C(CH}_3)_2\text{]}_6\text{-CH}_3$	105.56	448	4.08
62	G6	$\text{CH}_2\text{=C(CH}_3\text{)-[CH}_2\text{-C(CH}_3)_2\text{]}_6\text{-CH}_2\text{C(CH}_3\text{)=CH}_2$	106.51	432	1.35
63	A8	$\text{H-[CH}_2\text{-C(CH}_3)_2\text{]}_8\text{-CH}_3$	109.25	464	2.08
64	E7	$\text{CH}_2\text{=C(CH}_3\text{)-CH=C(CH}_3\text{)-[CH}_2\text{-C(CH}_3)_2\text{]}_7\text{CH}_3$	110.42	488	0.46
65	C7	$\text{CH}_3\text{-CH=CH-C(CH}_3)_2\text{-[CH}_2\text{-C(CH}_3)_2\text{]}_7\text{-CH}_3$	118.87	490	0.81

The monomer accounts for only about 9% of the pyrolysate of poly(isobutylene) as seen in the chromatogram performed on a Carbowax type column. Other fragments result from the cleavages in different points of the backbone and also from the elimination of side chain methyl groups. In addition to the compounds seen in Table 6.1.11, molecules with larger number of carbons atoms are typically generated during pyrolysis, together with some char and hydrogen. These compounds are not seen in the specific conditions of the analysis performed for the chromatogram displayed in Figure 6.1.25, which does not account for all molecular fragments generated during pyrolysis.

- Other polyolefins

Other homopolymers of olefins are used in practice, a larger side chain typically leading to materials adequate to be used in adhesives, wax coatings, and elastomers. More frequently, practical applications are known for the copolymers of these compounds with ethylene or in synthetic rubbers with butadiene or with isoprene. The decomposition products of some of the homopolymeric olefins when heated in an inert atmosphere are indicated in Table 6.1.12.

TABLE 6.1.12. Summary regarding literature information on thermal decomposition of several other polyolefins.

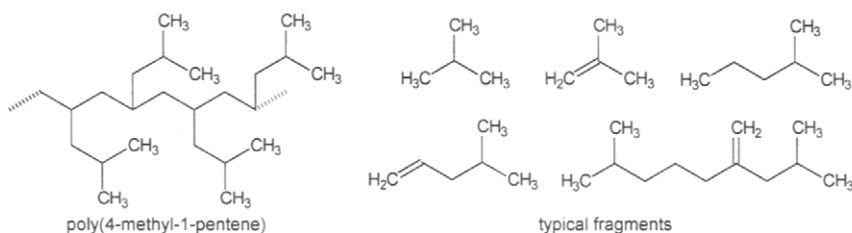
Polymer	Temp. °C	Results	Ref.
poly(3-methyl-1-butene)	Curie point	monomer, dimer	125
poly(3-methyl-1-pentene)	Curie point	monomer, dimer	125
poly(4-methyl-1-pentene)	291–341	after 22 hours at 341° C, 20% residue, 71% saturated and chain fragments; 9% of products volatile at 25° C, comprising isobutene (56%), propane (34%), traces of monomer, and hydrocarbons	126
poly(butene)	400–900	monomer, oligomers	127–129

TABLE 6.1.12 (continued). *Summary regarding literature information on thermal decomposition of several other polyolefins.*

Polymer	Temp. °C	Results	Ref.
poly(isopropenyl-cyclohexane)	400–900	methylenecyclohexane and/or methyl-1-cyclohexene, ethylcyclohexane, toluene, isopropenylcyclohexane, isomer of isopropenylcyclohexane, ethyl benzene, isopropylcyclohexadiene, pentadienylcyclohexane (5 isomers), dicyclohexylpropane, 3-cyclohexenyl-1-cyclohexylpentadiene, dicyclohexylhexadiene	130
poly(vinylcyclo-hexane)	335–391	small amounts of cyclohexane, cyclohexene, methylcyclohexene, methylcyclohexane, vinylcyclohexene, vinylcyclohexane, ethylcyclohexane with larger chain fragments	131, 132
poly(vinylcyclo-hexane)	360–380	cyclohexane (main product), cyclohexene, vinylcyclohexane, vinylcyclohexane oligomers, methane, ethane, ethylene, propane, propylene, butane, butylene, hydrogen	133

The pyrograms of longer side chain polyolefins may have a quite irregular aspect since the compounds forming the pyrolysate are generated through fragmentation that occurs in both the backbone and in the side chain. This is different from polyethylene where the pyrogram has good regularity consisting mainly of triplets (alkane, alkene, alkadiene) of compounds with the same carbon number.

An example of a branched polymer used as a synthetic elastomer is poly(4-methyl-1-pentene), CAS# 25068-26-2 [134]. The idealized structure of poly(4-methyl-1-pentene) and the formulas of a few molecular fragments found in the pyrolysate of this polymer are shown below:



A pyrogram for this polymer is shown in Figure 6.1.27. The pyrolysis and the separation of the pyrolysate were done in identical conditions as for the other polymers previously discussed, using 0.4 mg material pyrolysis at 600° C in He with separation on a Carbowax column (see also Table 4.2.2). The peak identification for the chromatogram shown in Figure 6.1.27 was done using MS spectral library searches and is given in Table 6.1.13.

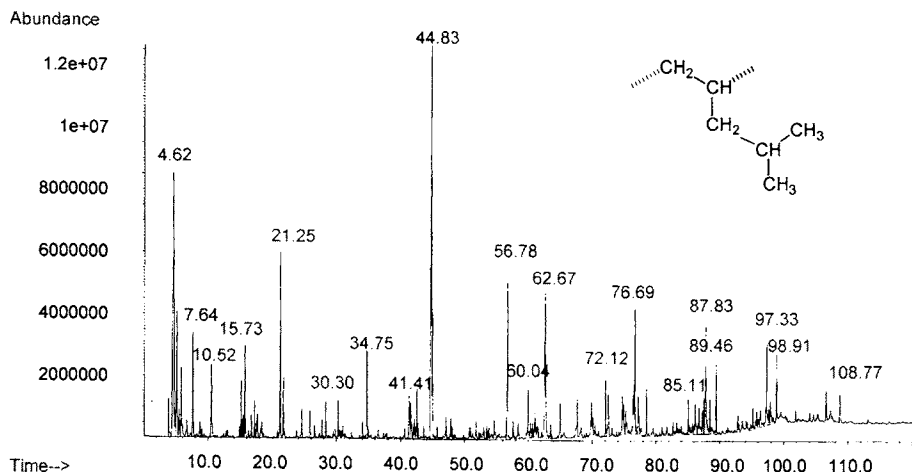


FIGURE 6.1.27. Result for a Py-GC/MS analysis of a high M_w sample of poly(4-methyl-1-pentene). Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

The compounds identified in the pyrolysate are alkanes, alkenes and alkadienes. However, the distinction based on the mass spectra between the different isomers for hydrocarbons with a larger number of carbon atoms is not simple, and a number of peaks in the chromatogram remained unnamed. The assignment of a given mass spectrum to a specific hydrocarbon can be done in some instances only tentatively. One example is the spectrum for the peak eluting at 44.83 min., which can be assigned to 2,4-bis(2-methylpropyl)-8-methyl-1-nonene, the trimer of 4-methyl-1-pentene. This spectrum is shown in Figure 6.1.28.

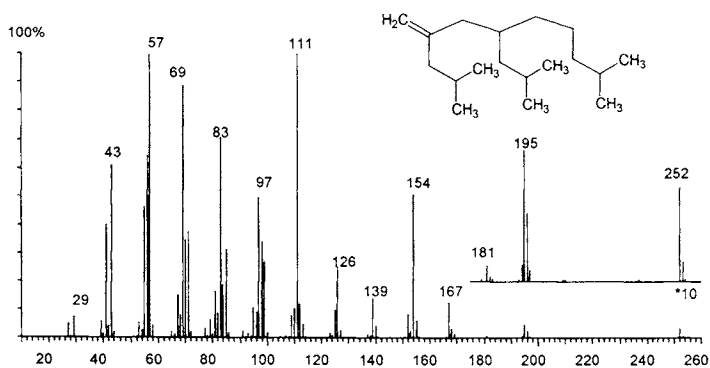


FIGURE 6.1.28. Mass spectrum tentatively assigned to 2,4-bis(2-methylpropyl)-8-methyl-1-nonene, the trimer of 4-methyl-1-pentene ($MW = 252$).

TABLE 6.1.13. Compounds identified in the pyrogram of poly(4-methyl-1-pentene) as shown in Figure 6.1.27.

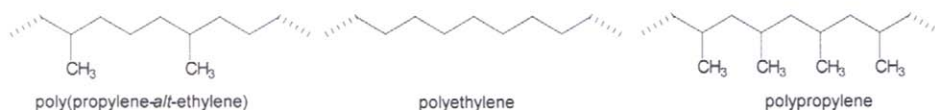
Peak	Compound	Ret. Time	MW	Area %
1	2-methylpropane	4.48	58	3.03
2	2-methyl-1-propene	4.62	56	8.75
3	2-methylpentane	4.92	86	0.43
4	4-methyl-1-pentene	5.12	84	3.20
5	2-methylhexane	5.51	100	0.76
6	2,4-dimethyl-1-pentene	5.84	98	1.96
7	2-methylheptane	6.73	114	0.58
8	6-methyl-1-heptene	7.64	112	2.53
9	2,4-dimethylheptane ?	8.77	128	0.43
10	2-methyl-1-nonene	10.53	140	1.82
11	2,7-dimethyl-1-octene	15.19	140	1.07
12	2-methyl-1-decene	15.45	154	0.38
13	2-methyldecane	15.73	156	1.82
14	2-methyl-3-decene	16.77	154	0.44
15	2-methyl-3-undecene	17.28	168	0.67
16	C12 alkane	17.67	170	0.77
17	7-methyl-1-undecene	18.38	168	0.55
18	2,8-dimethyl-4-methylene-nonane	21.25	168	3.65
19	C13 alkene	21.73	182	1.36
20	C13 alkadiene	24.59	180	0.62
21	C12 alkadiene	25.82	166	0.67
22	10-methyl-1-undecene	27.73	168	0.37
23	2,10-dimethylundecane	28.35	184	0.81
24	C14 alkene	30.30	196	0.63
25	C15 alkene	34.11	210	0.37
26	C14 alkene	34.75	196	1.53
27	hydrocarbon	41.41		1.38
28	hydrocarbon	41.62		1.06
29	C17 alkene	42.57	238	1.09
30	C18 alkene (tentatively assigned as a trimer)	44.83	252	10.68
31	C19 alkene	44.95	266	4.00
32	unknown hydrocarbon	47.10		0.76
33	unknown hydrocarbon	47.90		0.71
34	unknown hydrocarbon	51.84		0.41
35	unknown hydrocarbon	53.03		0.54
36	unknown hydrocarbon	53.49		0.25
37	unknown hydrocarbon	54.70		0.59
38	C20 alkene	56.78	280	4.00
39	C21 alkene	57.65	294	0.57
40	unknown hydrocarbon	58.43		0.50
41	C23 alkene	60.04	322	1.32
42	C24 alkene	60.37	336	0.42
43	C23 alkene	60.69	322	0.34
44	C23 alkene	61.09	322	0.77
45	C24 alkene	62.67	336	5.51
46	C26 alkene	62.81	350	0.42
47	C26 alkadiene	65.07	348	0.93
48	unknown hydrocarbon	67.70		1.10
49	unknown hydrocarbon	69.91		1.64
50	2,5-bis(1,1-dimethyl)-4-methylphenol (BHT)	72.12	220	1.05
51	C27 alkene	72.58	364	1.15

TABLE 6.1.13 (continued). Compounds identified in the pyrogram of poly(4-methyl-1-pentene) as shown in Figure 6.1.27.

Peak	Compound	Ret. Time	MW	Area %
52	unknown hydrocarbon	74.78		1.89
53	C27 alkene	75.32	364	0.72
54	C30 alkene	76.69	420	3.78
55	unknown hydrocarbon	77.29		1.10
56	C31 alkadiene	78.57	432	0.89
57	unknown hydrocarbon	85.11		0.81
58	unknown hydrocarbon	87.55		0.79
59	C36 alkadiene	87.83	502	2.75
60	C36 alkadiene	88.50	502	0.66
61	C37 alkadiene	89.46	516	1.44
62	C38 alkadiene	97.33	530	2.09
63	C39 alkadiene	98.91	544	1.28
64	unknown hydrocarbon	106.60		0.68
65	C38 alkadiene	108.77	530	0.74

The pyrolysis of poly(4-methylpentene) follows a similar path as that of other polyolefins. The strength for the C–C bonds in the side chain are not significantly different from those in the polymer backbone, and random fragmentations may occur equally for both. For this reason, the pyrogram shows low regularity, and fragments with a variety of chain lengths are seen in the pyrogram.

In the class of other homopolyolefins also can be included poly(propylene-*alt*-ethylene) or hydrogenated polyisoprene, CAS# 127883-08-3. The structure of the polymer is indicated below, together with that of polyethylene and polypropylene, shown for comparison.



The fragmentation of this polymer is expected to take place similarly to that of other saturated polyolefins. However, since the polymer does not have blocks of polyethylene or polypropylene, and the position of the methyl substituents on the carbon chain backbone is specific for this polymer, the pyrogram is expected to be different from that of polyethylene or polypropylene. A pyrogram for multi-arm poly(propylene-*alt*-ethylene) or hydrogenated polyisoprene (0.2% antioxidant) obtained in identical conditions as those for polyethylene or polypropylene is shown in Figure 6.1.29. The peak identification for the chromatogram shown in Figure 6.1.29 was done using MS spectral library searches and is given in Table 6.1.14.

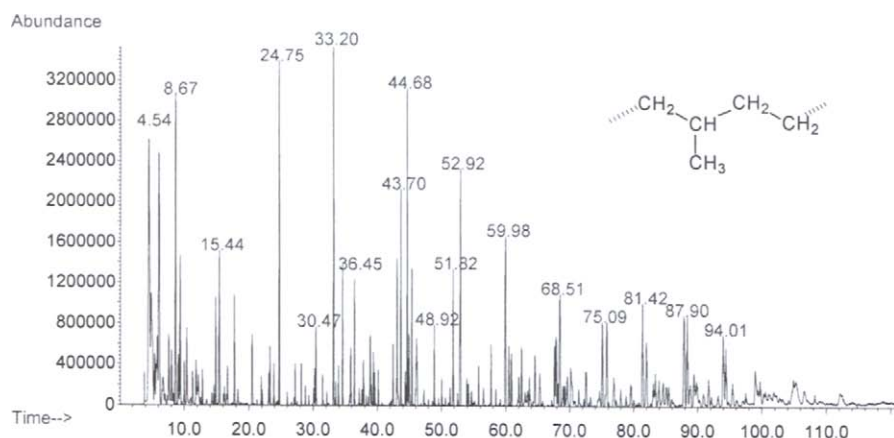


FIGURE 6.1.29. *Py-GC/MS results for multi-arm poly(propylene-alt-ethylene). Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.*

TABLE 6.1.14. *Compounds identified in the pyrogram of poly(propylene-alt-ethylene) as shown in Figure 6.1.29.*

Peak	Compound	Ret. Time	MW	Area%
1	1-propene	4.44	42	4.40
2	2-methylpropane	4.60	58	2.30
3	2-methylpropane	4.72	56	2.30
4	2-methyl-1-butene	4.92	70	2.30
5	3-methyl-1-pentene	5.02	84	2.07
6	methylcyclopentane	5.44	84	0.93
7	2-methyl-1-pentene	5.66	84	0.65
8	1,3-pentadiene	5.88	68	1.42
9	4-methylhexene	6.12	98	5.19
10	4-methyl-1-heptene	7.65	112	1.13
11	1,3-dimethylcyclohexane	8.09	112	0.79
12	2-methyl-heptene	8.67	112	5.48
13	2-methyl-3-heptene	9.14	112	0.86
14	3-methyloctane	9.38	128	2.39
15	3-methyl-1-octene	10.03	126	0.63
16	2,6-dimethyl-1-heptene	10.41	126	1.30
17	2,6-dimethyloctane	11.36	142	0.63
18	propylene trimer	11.42	126	0.63
19	3-methylenonane	11.85	140	0.63
20	4-methylnonane	12.80	142	0.63
21	4-propylheptane	14.88	142	1.39
22	2,6-dimethyloctene	15.44	140	2.06
23	2,5-dimethylnonene	17.77	154	1.42
24	2-methyl-5-methylenonane	20.53	154	0.78
25	C ₁₁ ;1	23.30	152	0.65
26	4-methylundecene ?	24.75	168	4.12
27	C ₁₃ ;1	30.47	182	0.88

TABLE 6.1.14 (continued). Compounds identified in the pyrogram of poly(propylene-alt-ethylene) as shown in Figure 6.1.29.

Peak	Compound	Ret. Time	MW	Area%
28	3-hexyl-1,1-dimethylcyclopentane ?	33.20	182	4.33
29	2,5-dimethyldodecane	34.61	198	1.51
30	C14;1	35.86	196	0.70
31	1,1,2,trimethylcycloundecane	36.45	196	1.31
32	C15	37.85	212	0.48
33	C15;1	38.91	210	0.88
34	1-ethenyl-3-methylbenzene	39.40	118	0.62
35	unknown [95(100), 69(100), 109(97), 55(96), 68(84),...194(5)]	42.45		0.69
36	C15;1	43.07	210	1.62
37	C15;cyclo	43.70	210	2.39
38	1-ethenyl-3-ethylbenzene	44.68	132	3.66
39	C16	44.96	226	0.88
40	1-ethenyl-4-ethylbenzene	45.39	132	1.46
41	C16;1 mix	46.11	224	0.36
42	C16;1	48.92	224	0.89
43	C16;2	51.82	222	1.72
44	C17;1	52.92	238	3.73
45	C18;1	57.72	252	0.72
46	C18;1	59.98	252	3.18
47	C18;1	60.49	252	0.93
48	C19	60.94	268	0.96
49	C19;1	62.47	266	1.11
50	C19;1	64.58	266	1.10
51	C19;1	65.35	266	0.00
52	C19;2	67.68	264	1.12
53	C20;1	67.93	280	1.50
54	C20;1	68.43	280	1.16
55	C20;1	68.51	280	1.15
56	C21;1, mix	70.20	294	0.00
57	C21;2	75.09	292	0.96
58	C21;2	75.17	292	0.90
59	C22;1	75.76	308	1.19
60	C22;1	75.86	308	0.95
61	C23;1	81.42	322	2.20
62	C23;2	82.00	320	0.44
63	C25;1	87.90	350	2.46
64	C25;1	88.40	350	0.84
65	C26;2	94.01	362	1.29
66	C27;1	94.41	378	0.64

As shown in Table 6.1.10, the pyrolysate contains alkanes, alkenes, some alkadienes and cycloalkanes (as identified by the MS library search). As expected, the comparison of the retention times in Table 6.1.10 with those from Table 6.1.1 and Table 6.1.8 shows that the compounds in the three pyrolysates, although all hydrocarbons, are not similar. This is also illustrated in Figure 6.1.30, which shows a time window from 20 min. to 40 min. of the pyrograms for poly(propylene-alt-ethylene) and for polyethylene and polypropylene.

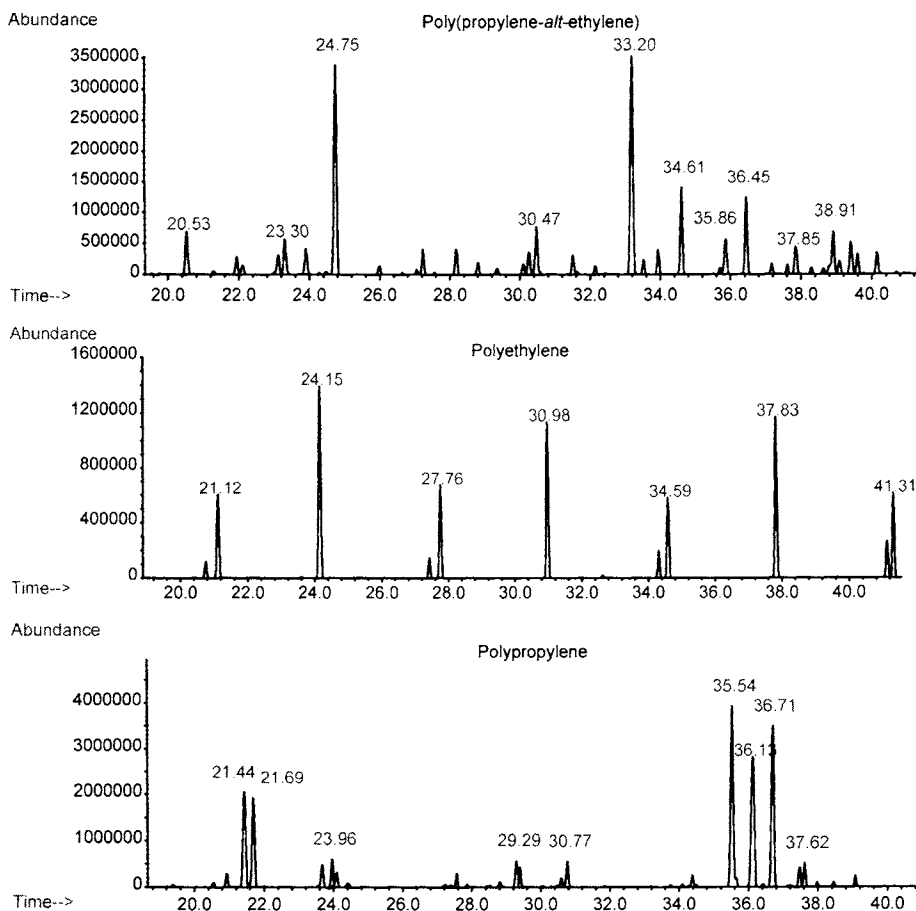


FIGURE 6.1.30. Time window from 20 min. to 40 min. of the pyrograms for poly(propylene-alt-ethylene) as shown in Figure 6.1.29, polyethylene as shown in Figure 6.1.1, and polypropylene as shown in Figure 6.1.16.

The pyrolysate of this *alt*-copolymer is different from that of *random*-copolymers or *block*-copolymers of ethylene with propylene.

- Copolymers of other olefins

Several copolymers of olefins with longer chain are used in practice. Among these, butyl rubber is probably the most commonly utilized. This material is a copolymer of isobutylene with small amounts of isoprene (1–6% wt). The amount of isoprene determines the extent of crosslinking. Pyrolysis of butyl rubber generates mainly products similar to those found in the pyrolysis of poly(isobutylene) including monomer, dimer, up to hexamers, depending on the pyrolysis temperature [135–137]. Besides the

decomposition performed exclusively under the influence of heat, the thermo-oxidative decomposition of butyl rubber also has been studied [138]. Also, other studies on qualitative or quantitative analysis of copolymers of olefins has been reported in literature [1, 112, 139–141], etc.

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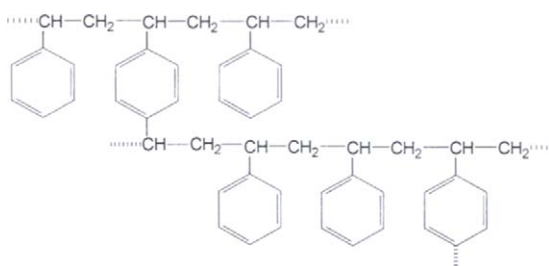
6.2 POLYSTYRENES

- General aspects

Polystyrenes form another class of polyhydrocarbons. The polymers from this class have many practical applications. The polystyrene type macromolecules have benzene groups attached on a saturated carbon chain. The most common polymer in the class is polystyrene (PS), which is obtained by the polymerization of styrene, usually in the presence of a peroxide initiator. Polystyrene has excellent characteristics necessary for use in commercial and industrial products, either as a pure material or in copolymers. These characteristics include the easy processing under injecting-molding, relatively good mechanical properties, transparency, good electrical insulating characteristics, etc. Polystyrene can be considered a vinyl polymer since the monomer has a phenyl attached to a vinyl group. However, polystyrenes are typically viewed as a separate class from other vinyl polymers. Polystyrenes with alkyl groups substituted on the benzene ring also are known in practice, but they have more limited applications. Besides polystyrene, another common polymer in this class is poly(α -methylstyrene), where alkyl (methyl) groups are attached to the backbone of the polymer at the same carbon atoms as the benzene ring.

- Polystyrene

Polystyrene (PS), CAS# 9003-53-6, is typically found in atactic and amorphous form. Isotactic and syndiotactic polystyrenes can be synthesized, but they are not used in practice since there are few advantages in properties compared to the atactic form. The reticulation of the carbon chains in polystyrene is frequently done using in the polymerization process a certain proportion of 1,4-divinylbenzene or less often of 1,3-divinylbenzene. The resulting polymer in the case of crosslinking with 1,4-divinylbenzene has the idealized structure shown below:



The general formula $[-\text{CH}(\text{C}_6\text{H}_5)-\text{CH}_2-]_n$ commonly used for PS corresponds to head to tail polymer (H-T), which is more common than head to head form (H-H). However, H-H polystyrene is known also, and in commercial products a certain proportion of H-H polymer can be present. Pure H-H polymer can be obtained using specific synthetic procedures [1].

A considerable number of papers describe the resulting molecules from the pyrolysis of polystyrene [2–26], etc. These studies include pyrolysis in inert conditions, in the presence of various catalysts [4], in the presence of carbon black [27], pyrolysis of H-T and H-H polymers, pyrolysis of polymers with different average molecular weights, pyrolysis of stereoregular polystyrene [28], pyrolysis of polystyrene obtained by controlled radical polymerization in the presence of 2,2,6,6-tetramethylpiperidine-N-oxyl (stable nitroxide) [29], pyrolysis in the presence of water in subcritical conditions [30], pyrolytic studies for the understanding of large scale processes [31–36], etc.

Thermal degradation of polystyrene involves depropagation and first order termination [37]. Initial decomposition temperature is $300\text{--}330^\circ$ [38]. The kinetics of the decomposition follows the general rule $d\alpha/dt = k(1 - \alpha)[1 - (1 - \alpha)^{2b}]^{1/2}$ where α is the conversion (and equal to the ratio of the volatilized mass to the initial mass), k is the overall rate constant, and b is a parameter depending on the pyrolysis temperature. The overall activation energy for the decomposition is 43 kcal mol^{-1} [39, 40]. The curve showing the variation of weight loss % as a function of temperature (TG curve) for a 3.5 mg PS sample with $M_w = 280,000$ is shown in Figure 6.2.1.

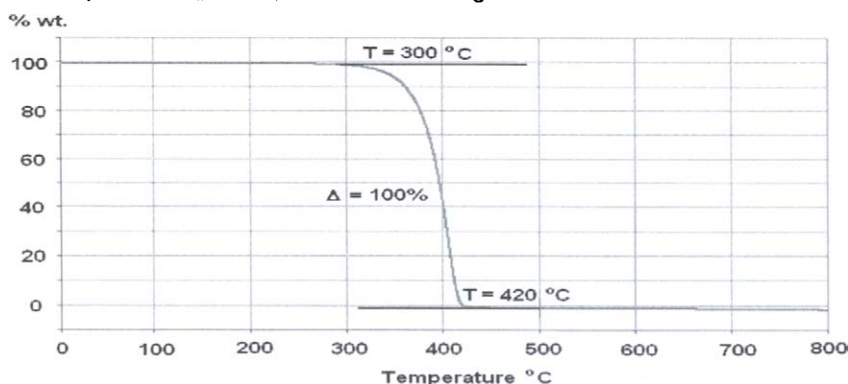
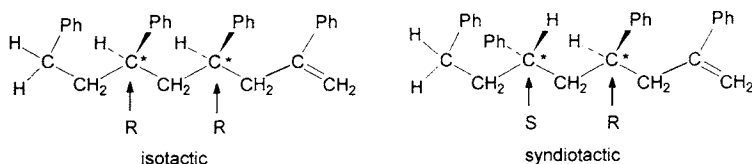


FIGURE 6.2.1. Variation of weight % loss for a polystyrene sample in a TGA experiment at a heating rate of 10°C/min .

The heating was done in air between 30° C and 830° C at a rate of 10° C/min. The TGA shows that polystyrene starts decomposing around 300° C and does not leave a noticeable char residue. The rate of degradation is influenced by the method of synthesis of PS [37]. Anionically initiated polystyrene is more stable thermally than that produced by thermal initiation or with free-radical initiators, e.g. benzoyl peroxide or azoisobutyronitrile. During heating, after about 10% weight loss all polystyrene polymers degrade at about the same rate [41] with an activation energy $E_{act} = 188 \text{ kJ mol}^{-1}$ in vacuum or in flowing nitrogen [42, 43].

Among other findings regarding PS pyrolysis, it has been shown that the polymers with higher molecular mass compared to those with lower molecular mass give a higher yield of monomer [15, 44]. Differences also were found in the pyrolysates for the H-T polymer compared to H-H polymer [3] (see Section 4.3).

For the differentiation between an isotactic polystyrene and the syndiotactic material, it is necessary to investigate the tetramer (or higher) fragments present in a pyrogram, in the same manner as it was shown for polypropylene. The tetramer fragments from isotactic polystyrene and syndiotactic polystyrene are diastereoisomers and can be separated by GC on a nonchiral column [45]. The two chiral centers are in this case (R,R) and (S,R) as shown in the following formulas:



The relative intensities of the tetramer and pentamer diastereoisomers can be used for the evaluation of the tacticity of common polystyrene [28]. The increase in the pyrolysis temperature diminishes the content of tetramer and pentamer in the pyrolysate, favoring smaller fragments. The errors in the estimation of small peak areas increase, and the procedure using these fragments for tacticity estimation is sometimes difficult.

The results for other conditions for polystyrene pyrolysis were reported. For example, pyrolysis on different catalysts was shown to lead to modifications of the yield of specific components in the pyrolysate. During the pyrolysis of PS on solid acid catalysts, the increase of contact time and surface acidity enhanced the production of ethylbenzene. Pyrolysis in the presence of water increases the yield of volatile products and that of monomer [30]. Studies on the generation of polycyclic aromatic hydrocarbons (PAHs) in polystyrene pyrolysates also were reported [36]. It was demonstrated that the content in PAHs in polystyrene pyrolysates increases as the pyrolysis temperature increases. The analysis of the end groups in polystyrenes with polymerizable end groups (macromonomers) was reported using stepwise pyrolysis and on-line methylation [46].

Oxygen plays a very important role in the degradation of polystyrene. The activation energy for the thermal degradation above 350 °C decreases to 90 kJ mol⁻¹ in the presence of an excess of oxygen [47]. The degradation mechanism involves depropagation. Thermal-oxidative products include benzaldehyde, benzoic acid,

acetophenone, phenol, benzyl alcohol, cinnamaldehyde, styrene, styrene dimer (diphenyl butene) and styrene trimer (triphenyl hexene). Antioxidants retard oxidative degradation by scavenging peroxy radicals as they are formed. A summary of various other reports regarding thermal degradation of polystyrene are summarized in Table 6.2.1 [48].

TABLE 6.2.1. Summary regarding literature reports on thermal decomposition of polystyrene.

Polymer	Temp. °C	Results	Ref.
head-to head polystyrene	320	monomer, dimer, trimer, tetramer, pentamer, stilbene	49
head-to head polystyrene	500 under N ₂	hydrocarbons (C ₁ -C ₄) (2.2 relative GC peak intensity), benzene (0.4), toluene (3.3), ethylbenzene (2.0), styrene (20.4), 3-phenyl-1-propene (1.5), 1-phenylpropane (2.3), α -methylstyrene (0.3), 1-phenylbutadiene (1.0), diphenylmethane (0.3), 1,1-diphenylethylene (2.6), 1,2-diphenylethane (1.3), 1,2-diphenylpropane (0.7), 1,2-diphenyl-1-propene (0.5), 2,3-diphenyl-1-propene (2.2), 3,4-diphenyl-1-butene (0.5), 2,3-diphenylbutadiene (2.0), 1,2-diphenylethylene (6.5), 1,4-diphenylbutane (3.5), 1,4-diphenyl-1-butene (3.8), 1,4-diphenyl-1-pentene (1.3), 1,3-diphenylpropadiene (2.1), 1,2-diphenylbutadiene (1.8), 1,4-diphenylbutadiene (1.9), 1,3,4-triphenylbutene (0.6), 1,2,5-triphenyl-pentene (1.5), 1,2,5-triphenyl-1-pentene (4.6), 2,3,6-triphenyl-1-hexene and 2,5,6-triphenyl-1-hexene (8.9), 1,4,5-triphenyl-1-pentene (4.4)	50
head-to head polystyrene	ambient to 600	styrene, 1,2-diphenylethene, 1,2-diphenylpropane, 1,4-diphenylbutane, 1,4-diphenyl-1-butene, 1,4-diphenylpentane, 4,5-diphenyl-1,8-octadiene, 2,3,6-triphenyl-1-hexene, 1,4,5-triphenyl-1-pentene	51
poly(α -deuterostyrene)	334–387	68.4% monomer, 1.5% α -deuterostyrene, 0.6% α -methylstyrene, 29.5% larger chain fragments	52, 53
poly(β -deuterostyrene)	345–384	39.7% monomer, 1.2% toluene, 0.1% deuterotoluene, 59% larger chain fragments	52, 53
polystyrene	300–400	40.6% monomer, 2.0% toluene, 0.1% CO, remainder dimer, trimer, and tetramer; the monomer yield increases with the pressure of nitrogen to 62% at 1013 mbar	54, 55
polystyrene	500–600	monomer, dimer and trimer with small amounts of toluene, α -methyl styrene and 1,3-diphenylpropane	56, 57
polystyrene	500–1200	small hydrocarbon fragments (C ₁ -C ₆); fragmentation is greater the higher the temperature and the greater the pressure of inert gas	58
polystyrene	300–570	pulsed pyrolysis and 40 μ g of polymer; styrene (92.4-99.8% depending upon temperature), benzene, toluene, and ethyl benzene	59
polystyrene	ambient to 500	thin films (1000 Å or less), monomer yield about 55%	60
polystyrene	500 flash in He	benzene, toluene, ethylbenzene, styrene, indane, (1-methyl-vinyl)benzene, xylenes, indene, methylindene, (1-methyl-1-propenyl)benzene, (2-phenylethyl)benzene, (1-methyl-2-phenylethyl)benzene, (1-benzylvinyl)benzene, (3-phenylpropyl)benzene, divinylbenzene, (3-phenyl-2-propenyl)benzene, (1-methyl-3-phenyl-2-propenyl)-benzene, (1-methylene-3-phenyl-2-propenyl)-benzene,	2

An example of a pyrogram of a polystyrene sample ($M_w = 280,000$) is shown in Figure 6.2.2. The pyrolysis was done at 600° C in He with separation of a Carbowax column and MS detection, similarly to other polymers discussed in this book (see also Table 3.4.1). The peak identification for the chromatogram shown in Figure 6.2.2 was done using MS spectral library searches only and is given in Table 6.2.2.

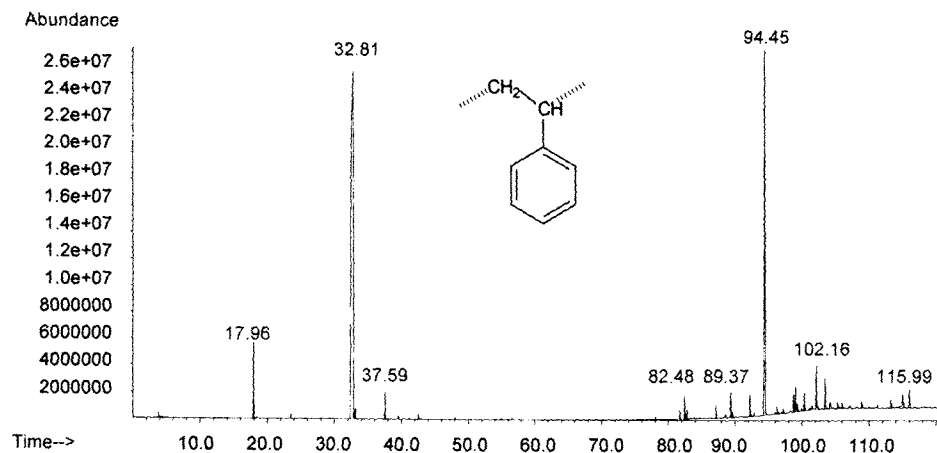


FIGURE 6.2.2. Result for a Py-GC/MS analysis of polystyrene. Pyrolysis done on 0.4 mg material with $M_w = 280,000$ at 600°C in He, with the separation on a Carbowax type column.

TABLE 6.2.2. Compounds identified in the pyrogram of polystyrene shown in Figure 6.2.2.

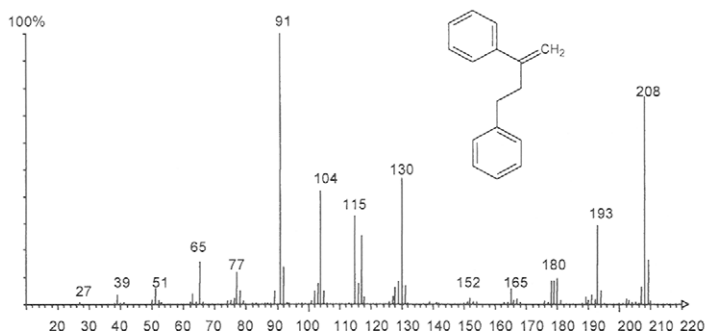
Peak	Compound	Ret. Time	MW	Area %
1	benzene	12.68	78	trace
2	toluene	17.96	92	2.93
3	ethylbenzene	23.52	106	0.31
4	ethenyl benzene (styrene)	32.81	104	55.06
5	1-propenylbenzene	33.15	118	0.39
6	α -methylstyrene (1-methylethenyl)benzene	37.59	118	1.01
7	3-butenylbenzene	39.68	132	trace
8	2-propenylbenzene	42.59	118	0.21
9	indene	47.99	118	trace
10	biphenyl	76.50	154	low trace
11	1,1'-(1-methyl-1,2-ethandiyl)bis-benzene	81.76	196	0.37
12	1,1'-(1,2-ethandiyl)bis-benzene	82.48	182	0.94
13	1,1'-ethenylidenebis-benzene	82.85	180	0.36
14	(Z)-1,1'-(2-butene-1,4-diyl)bis-benzene	87.18	208	0.51
15	1,1'-(1,3-propandiyl)bis-benzene	89.37	196	1.25
16	1,1'-[1-(2-propenyl)-1,2-ethandiyl]bis-benzene	89.67	222	trace
17	2,4-diphenyl-1-pentene	92.24	222	0.96
18	(3-phenylbut-3-enyl)benzene or styrene dimer	94.45	208	23.53
19	(E)-1,1'-(butene-1,4-diyl)bis-benzene	96.31	208	0.36
20	1,2,3,4-tetrahydro-1-phenylnaphthalene	97.19	208	0.31
21	1,1'-cyclopropylidenebis-benzene	98.73	194	0.88
22	unknown [219(100), 220(84), 103(29), 77(26), 143(22)]	99.06	220	0.98
23	2,5-diphenylhex-1-ene	99.35	236	0.38
24	1,1'-(1,2-ethenediyl)bis-benzene	100.37	180	0.75
25	(Z)-1,1'-(1-butene-1,4-diyl)bis-benzene	102.16	208	2.04
26	2,5-diphenyl-1,5-hexadiene	103.48	234	1.43
27	2,5-diphenylhex-3-ene	104.15	236	0.59
28	1,4-diphenyl-1,3-butadiene	104.33	206	trace

TABLE 6.2.2 (continued). *Compounds identified in the pyrogram of polystyrene shown in Figure 6.2.2.*

Peak	Compound	Ret. Time	MW	Area %
29	2,3,5-trimethylphenanthrene ?	105.33	220	0.33
30	1,5-diphenyl-1,5-hexadiene	106.03	234	0.31
31	1,5-diphenyl-1,3-pentadiene	108.88	220	0.42
32	unknown [220(100), 219(98), 143(20), 91(22), 128(16)]	113.23	220	0.54
33	1,3-diphenyl-1,5-hexadiene	115.01	234	1.63
34	1,1-diphenyl-1,3-pentadiene ?	116.00	220	1.22

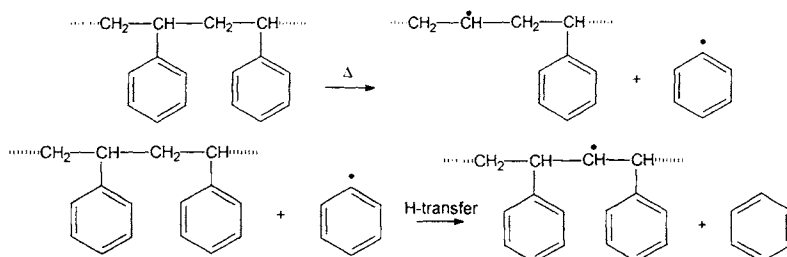
The list of compounds generated in polystyrene thermal decomposition shown in Table 6.2.2 do not include char and hydrogen. However, both char (mostly carbon) as well as hydrogen result in polystyrene pyrolysis, mainly at higher temperatures and at high heating rates [6].

Most compounds from the pyrogram have spectra available in common mass spectral libraries. However, the spectrum of (3-phenylbut-3-enyl)benzene is not present in common libraries and is shown in Figure 6.2.3.

FIGURE 6.2.3. *Mass spectrum of (3-phenylbut-3-enyl)benzene (styrene dimer).*

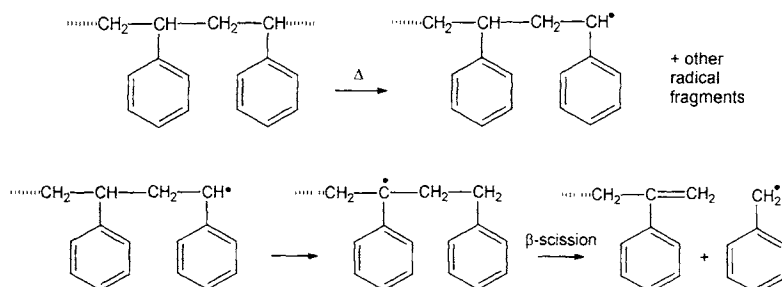
The list of compounds in Table 6.2.2 indicates a higher proportion of monomer than the one given in Table 2.1.1 that is 42% monomer. The value in Table 6.2.2 is higher because it is given relative to the compounds seen in the chromatogram (volatiles) and does not account for all components in the pyrolysate.

The mechanism of pyrolysis of polystyrene was discussed in Section 2.1 in relation with the description of general mechanisms encountered in pyrolysis. The formation of traces of benzene, toluene, etc in the pyrolysate is also discussed in literature [15, 40, 61, 62]. Although they account for only a very small proportion of the molecules formed during pyrolysis, some side chain scissions may occur as shown below:



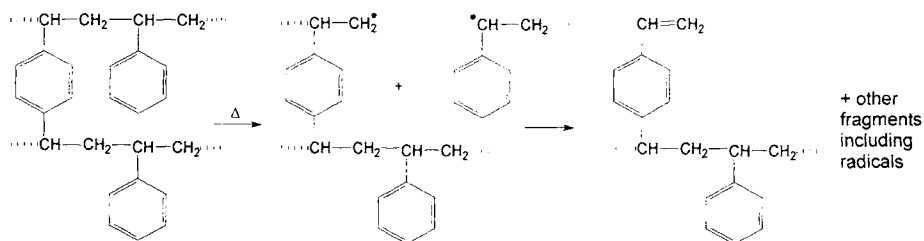
Phenyl radicals are indeed formed during polystyrene pyrolysis, as proven by low traces of biphenyl present in the pyrolysate.

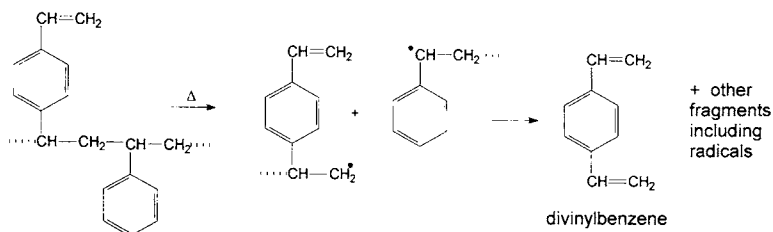
A radical transfer reaction also occurs in a small proportion, leading to the formation of toluene as shown in the following scheme:



The benzyl radical can further generate toluene by an H-transfer reaction.

The degree of reticulation with divinylbenzene in polystyrene can be estimated from analytical pyrolysis results. The following set of reactions indicates some random scissions of the polymer followed by β -scissions that lead to the formation of 1,4-divinylbenzene present in the pyrolysate of crosslinked polystyrene:





Several studies on thermal degradation products of polystyrene crosslinked with divinylbenzene are reported in literature. Poly(styrene-co-divinylbenzene) heated between 385° C and 450° C generates volatile products including toluene, benzene, styrene, and xylene [63, 64]. Polystyrene crosslinked with increasing quantities of divinyl or trivinyl benzene heated between 346° C and 450° C shows a decrease in the styrene yield with increasing quantities of divinyl or trivinyl benzene. The yield of larger chain fragments and the amount of carbonization also increase. Poly(styrene-co-trivinylbenzene) heated between 470° C and 500° C generates a mixture of aliphatic and aromatic hydrocarbons [63, 64].

Oxygen plays a very important role in the thermal degradation of polystyrene. The activation energy for the thermal degradation of polystyrene above 350° with an excess of oxygen decreases (from 188 kJ mol⁻¹) to 90 kJ mol⁻¹ [38]. Degradation mechanism in the presence of oxygen also involves depropagation. Antioxidants retard oxidative degradation by scavenging peroxy radicals as they are formed. Pyrolysis in the presence of ammonium perchlorate also has been reported [12]. Several compounds reported in the pyrolysates of polystyrene in air when the material is heated between 385° C and 450° C include benzaldehyde, benzoic acid, acetophenone, phenol, benzyl alcohol, cinnamaldehyde, styrene, styrene dimer (diphenyl butene) and styrene trimer (triphenyl hexene) [38].

- Copolymers of styrene

A large number of copolymers of styrene are used in practice, some of them with very large industrial production. Both binary and ternary copolymers have been synthesized, their structure being adapted to cover a range of properties. These copolymers can have different structures such as *random*, *block*, *graft*, *star*, etc. Some of the copolymers are thermoplastic materials and some are elastomers. A variety of additives are used in these copolymers, including antioxidants, fillers, reinforcing materials, additives necessary for the manufacturing process, etc.

Styrene copolymer with divinylbenzene is used frequently in many polystyrene products, and the similarity between the two comonomers makes this copolymer almost identifiable with the homopolymer itself. In terms of production volume, styrene copolymer with butadiene is probably the most important copolymer (SBR). Depending on the butadiene/styrene ratio, the copolymer is used as an elastomer with large applications in the tire industry, in the manufacturing of conveyor belts, etc. when butadiene/styrene ratio is 75/25 parts wt., or when butadiene/styrene ratio is 40/60 parts

wt. with applications in latex paints, adhesives, etc. Several production procedures are known, including radical polymerization (using e.g. potassium persulfate as an initiator) in an emulsion at 50 °C (hot rubber procedure) or at 5 °C (cold rubber) using more active initiators such as cumene hydroperoxide or *p*-menthane hydroperoxide. The broader MW distribution obtained from hot rubber process leads to materials more suitable for adhesives. The "cold" product has more *trans* isomer (72%). Polymerization using anionic catalysis such as alkyl lithium leads to more control over molecular structure generating a higher content of *cis* isomer, which imparts better elasticity.

Styrene and butadiene also form copolymers known as high impact polystyrene, or rubber-modified polystyrene, when the content of butadiene is 5–10%. This type of material has excellent mechanical properties, and it is widely used in practice for the manufacturing of numerous objects, including parts for household appliances, furniture, etc. Rubber-modified polystyrene is commonly used as wood replacement and also for packaging. The synthesis of this material typically is done by dissolving polybutadiene in styrene monomer, followed by free radical polymerization achieved using a peroxide catalyst. This procedure leads to block or graft type copolymers.

Styrene and isoprene also may copolymerize and give a variety of products including random, diblock, triblock and star copolymers. These copolymers also are used as elastomers in the tire industry, but are less common compared to SBR.

One other common styrene copolymer is poly(styrene-*co*-acrylonitrile) (SAN). This material is used in the manufacturing of various household appliances and goods, automotive parts, etc. The copolymer can be synthesized by free radical polymerization, either using emulsion, suspension or continuous bulk polymerization. The polymer has good heat and impact resistance. For the alternating copolymer, the weight loss begins to be noticed only at 323 °C [65]. The activation energy of decomposition is 142 kJ mol⁻¹, and the maximum rate of decomposition occurs at 425 °C with formation of NH₃ and HCN among other products [66]. The weight loss is smaller when heating occurs in N₂ rather than an air environment. Pyrolysis at 500 °C under N₂ produces HCN, acetonitrile, acrylonitrile, styrene and toluene among other products. The amount of HCN is proportional to the acrylonitrile content [67].

Another styrene copolymer is poly(methyl methacrylate-*co*-styrene), which can be used to strengthen the interfaces between immiscible homopolymers and is added in various polymer blends to improve their mechanical properties.

Styrene is frequently used as part of some terpolymers with large practical utilization. One such copolymer is acrylonitrile-butadiene-styrene terpolymer (ABS). Usually it is made as poly(1-butenylene-*graft*-1-phenylethylene-*co*-cyanoethylene). This form of the copolymer can be made by grafting styrene and acrylonitrile directly on to the polybutadiene latex in a batch or continuous emulsion polymerization process. Grafting is achieved by the free-radical copolymerization of styrene and acrylonitrile monomers in the presence of polybutadiene. The degree of grafting is a function of the 1,2-vinyl content of the polybutadiene, monomer concentration, extent of conversion, temperature and mercaptan concentration (used for crosslinking). The emulsion polymerization process involves two steps: production of a rubber latex and subsequent polymerization of styrene and acrylonitrile in the presence of the rubber latex to produce an ABS latex.

This latex is then processed to isolate the ABS resin. ABS thermoplastic combines good mechanical properties and heat resistance. It is used in many household appliances, automotive parts, furniture, etc. Another similar terpolymer is acrylonitrile-styrene-acrylate (ASA). It is used in automobile industry, in house construction, household appliances, etc.

Numerous other copolymers of styrene are known, such as poly(acrylonitrile-co-styrene-co-ethylene), or poly(methyl methacrylate-co-butadiene-co-styrene), which is utilized in making blister-packaging, disposable medical instruments, containers, etc. The frequent utilization of styrene copolymers in practice has been associated with a considerable number of studies regarding pyrolysis and thermal behavior of these copolymers [68–86]. Some of these studies are summarized in Table 6.2.3.

TABLE 6.2.3. Summary regarding literature reports on thermal decomposition of some styrene copolymers.

Polymer	Temp. °C	Results	Ref.
alkyne containing polystyrenes	500–550	random scission leading to monomer takes place for poly(<i>p</i> -phenylethynylstyrene) and poly(<i>p</i> -trimethylsilylethynylstyrene). Poly(<i>p</i> -ethynylstyrene) showed somewhat different degradation behavior. The terminal alkyne was very susceptible to cross-linking and the monomer was recovered in very low amount (1–3 wt.%, depending on the pyrolysis conditions).	87
high-impact polystyrene + brominated flame retardants		the brominated additives do not change the decomposition temperature of the polymer	88
poly(<i>p</i> -phenylethynylstyrene)	500–550	40% <i>p</i> -phenylethynylstyrene, <i>p</i> -xylene, <i>p</i> -ethyltoluene, and <i>p</i> -methylstyrene	87
poly(2-bromoethyl methacrylate-co-styrene) 50/50 mol/mol	ambient to 500	styrene, 2-bromoethyl methacrylate, modified chain fragment fraction. Minor products; ethylene, CO ₂ , HBr, vinyl bromide, acetaldehyde	89
poly(acrylonitrile-co-styrene) 0/100-50/50	292	acrylonitrile causes increase in rate of chain scission; proportion of acrylonitrile among degradation products greater than from pure polyacrylonitrile; chain fragments increase with acrylonitrile content of copolymer; styrene, acrylonitrile, toluene, benzene, four dimers, and four trimers	90
poly(acrylonitrile-co-styrene) 1.86-96.62 mol% A	500	HCN, acetonitrile, acrylonitrile, propionitrile, toluene, ethylbenzene, styrene, methane, ethylene, ethane, C ₃ hydrocarbons, but-1-ene, prop-1-ene-3-nitrile, isopropyl nitrile, benzene	91
poly(methyl methacrylate)-blend-poly(styrene)	ambient to 500	polymers degrade separately without interaction to give same products as polymers degraded separately; copolymers and mixtures of the same molar compositions can be distinguished by degradation behavior	92
poly(methyl methacrylate-co-styrene)	260–340	methyl methacrylate, styrene and oligomers of styrene; formation of oligomers of styrene strongly inhibited by presence of methyl methacrylate units	93
poly(<i>p</i> -trimethylsilylethynylstyrene)	500–550	80% monomer, trimethylsilylethynyl derivatives of benzene, toluene, ethylbenzene, and methylstyrene	87

TABLE 6.2.3 (continued). Summary regarding literature reports on thermal decomposition of some styrene copolymers.

Polymer	Temp. °C	Results	Ref.
poly(styrene) 1/1 w/w blend bisphenol A polycarbonate	ambient to 500	CO ₂ , styrene, α -methylstyrene, p-cresol, phenol, p-ethylphenol, p-vinylphenol, p-isopropylphenol, polystyrene short chain fragments with vinylidene and saturated ends, polycarbonate cyclic dimer and chain fragments, bisphenol A	94
poly(styrene-co-1,2,2,2-tetrachloroethyl acrylate) 3.8/1	310 and 500	styrene, benzene, toluene, allylbenzene, α -methylstyrene, indane, isopropenylstyrene, 5,6-benzo-2-methyl-3,5-cyclo-hexadienone, propylpropenylbenzene, diphenylethane, 1,3-diphenylpropane, dimers and trimers of styrene, chloroacetaldehyde, dichloroacetaldehyde, trichloroacetaldehyde, trichloropropanal, benzyl chloride, 2-chloroethylstyrene, 2,2-dichloroethenyl methacrylate, 1,2,2,2-tetrachloroethyl methacrylate	95
poly(styrene-co-1,2,2,2-tetrachloroethyl acrylate) 4.7/1	310 and 500	styrene, benzene, toluene, ethylbenzene, α -methylstyrene, diphenyl, 5,6-benzo-2-methyl-3,5-cyclohexadienone, diphenylethane, 1,3-diphenylpropane, dimers and trimers of styrene, chloroacetaldehyde, dichloroacetaldehyde, trichloropropanal	95
poly(styrene-co-acrylonitrile)	400	calculation of kinetic parameters and sequence distribution	96
poly(styrene-co-acrylonitrile)	500	acrylonitrile, benzene, toluene, ethylbenzene, indane, indene, propenylbenzene, butenylbenzene, divinylbenzene, naphthalene, 2-(2-phenylethyl)-2-propenenitrile, vinylpyridine, [1-(2-phenylethyl)vinyl]benzene, quinoline, isoquinoline, indole	2
poly(styrene-co-bis-(1,2,2,2-tetrachloroethyl fumarate) 8.9/1	310 and 500	styrene, benzene, toluene, ethylbenzene, allylbenzene, α -methylstyrene, indane, diphenyl propylpropenylbenzene, diphenylethane, 1,3-diphenylpropane, dimers and trimers of styrene, chloroacetaldehyde, dichloroacetaldehyde, trichloroacetaldehyde, benzyl chloride	95
poly(styrene-co-bis-(1,2,2,2-tetrachloroethyl muconate) 7.72/1	310 and 500	styrene, benzene, toluene, ethylbenzene, α -methylstyrene, diphenyl, propylpropenylbenzene, diphenylethane, 1,3-diphenylpropane, dimers and trimers of styrene, chloroacetaldehyde, dichloroacetaldehyde, trichloroacetaldehyde, trichloropropanal, benzyl chloride	95
poly(styrene-co-chlorotrifluoroethylene) 7.7, 14, 20 mol% CTFE	ambient to 500	chlorotrifluoroethylene, styrene, HCl, chloropentafluoropropene, ethene, chloroethene, toluene, α -methylstyrene, dimer and trimer structures with some unsaturation; SiF ₄ (from reaction of HF with glass). Distribution of products varies with polymer composition	97
poly(styrene-co-glycidyl methacrylate) 10, 23, 51, 62, 78, 86 mol% GMA	ambient to 500	CO, CO ₂ , propene, isobutene, dimethyl ketene, acrolein, allyl alcohol, toluene, styrene, α -methylstyrene, ethylbenzene, glycidol, glycidylmethacrylate; product distribution depends on copolymer composition	98
poly(styrene-co-methacrylic acid) 18, 44, 72 mol% MAA	ambient to 500	CO ₂ , H ₂ O, butene, isobutene, dimethyl ketene, styrene, methacrylic acid, succinic-type 5-membered cyclic anhydrides	99
poly(styrene-co-methyl methacrylate)	560	percent ratio determined from decomposition results	100
poly(styrene-co-methyl methacrylate)	450–600	percent ratio determined from decomposition results	83

TABLE 6.2.3 (continued). Summary regarding literature reports on thermal decomposition of some styrene copolymers.

Polymer	Temp. °C	Results	Ref.
poly(styrene-co-methylene) ~CH(C ₆ H ₅)-(CH ₂) ₂ -CH(C ₆ H ₅)-(CH ₂) _n ~	350 for 4 hr.	benzene, toluene, ethylbenzene, styrene (major volatile product), n-propylbenzene (except with n = 2), phenylpropene, butylbenzene (except with n = 0), phenylbutene (with n = 4 and 5 only), amylbenzene (with n = 4 and 5 only), hexylbenzene (with n = 4 and 5 only), chain fragment fraction (major product)	101
poly(styrene-co-N-(2,4,6-tribromophenyl) maleimide) 6.4/1	310 and 500	styrene, benzene, toluene, ethylbenzene, allylbenzene, α-methylstyrene, indane, diphenylethane, 1,3-diphenylpropane, dimers and trimers of styrene, N-(2,4,6-tribromophenyl) maleimide, N-dibromophenyl maleinimide	95
poly(styrene-co-N-(pentachlorophenyl) maleimide) 4.9/1	310 and 500	styrene, benzene, toluene, ethylbenzene, allylbenzene, α-methylstyrene, indane, diphenylethane, 1,3-diphenylpropane, dimers and trimers of styrene, pentachlorophenyl isocyanate, N-pentachlorophenyl formamide, N-tetrachlorophenyl maleinimide, N-(pentachlorophenyl) maleimide, methyl maleic acid pentachlorophenylimide	95
poly(styrene-co-phenyl methacrylate) 10-90 mol% PMA	ambient to 500	CH ₄ , CO, CO ₂ , propene, dimethyl ketene, toluene, styrene, 4-phenylbutene, 4-phenyl-2-methylbutene, phenyl methacrylate, α-methylstyrene, short chain fragments	102
poly(styrene-co-vinyl acetate)	350-450	copolymers with 5-20% VA degrade in a single stage with styrene and acetic acid the main degradation products	103
poly(styrene-co-vinylcyclohexane)	500	study of diad sequence in the copolymer	74
poly(vinyl acetate)-blend-poly(styrene) 1/1 w/w	ambient to 500	products as for individual polymers	104
poly(vinyl acetate-co-styrene) 5-20 mol% VA	ambient to 500	acetic acid, styrene, chain fragment fraction, ketene, CO ₂	105
poly(vinyl chloride)-blend-poly(styrene)	ambient to 500	HCl, styrene	106
poly(vinyl chloride)-blend-poly(styrene) 10/1 to 1/10 w/w	ambient to 500	products as for individual polymers	107

Thermal properties and pyrolysis results of some copolymers including styrene as comonomer are discussed in this section, but also in Section 6.7 (see Figure 6.7.26), and in Section 7.1. One example of a pyrogram for a copolymer of styrene is shown in Figure 6.2.4 for poly(styrene-co-divinylbenzene) 2% cross-linked, CAS# 69011-14-9. The pyrolysis was done at 600° C in He with separation of a Carbowax column and MS detection, similarly to other polymers discussed in this book (see also Table 4.2.2). The peak identification for the chromatogram shown in Figure 6.2.4 was done using MS spectral library searches only and is given in Table 6.2.4.

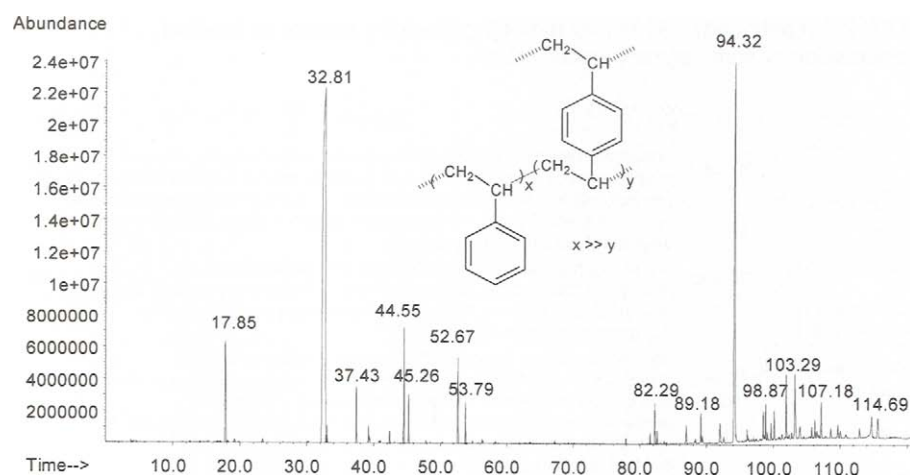


FIGURE 6.2.4. Result for a Py-GC/MS analysis of poly(styrene-co-divinylbenzene) 2% crosslinked. Pyrolysis done at 600° C in He, with the separation on a Carbowax type column.

TABLE 6.2.4. Compounds identified in the pyrogram of poly(styrene-co-divinylbenzene) 2% crosslinked, shown in Figure 6.2.4.

Peak	Compound	Ret. Time	MW	Area %
1	toluene	17.86	92	3.09
2	ethylbenzene	23.41	106	trace
3	styrene	32.81	104	48.52
4	1-propenylbenzene	33.04	118	0.36
5	α -methylstyrene (1-methylethenyl)benzene	37.43	118	1.42
6	1-vinyl-4-methylbenzene	39.26	118	0.40
7	3-butenylbenzene	39.41	132	trace
8	2-propenylbenzene	42.42	118	0.28
9	4-ethyl-1-ethenylbenzene	44.55	132	3.04
10	3-ethyl-1-ethenylbenzene	45.26	132	1.21
11	1H-indene	47.99	118	trace
12	1,4-divinylbenzene	52.67	130	2.20
13	1,3-divinylbenzene	53.79	130	1.01
14	1-phenyl-cyclohex-1-ene	54.84	158	trace
15	2-ethyl-1H-indene	56.28	144	trace
16	(3-methyl-1-methylenepentyl)benzene ?	67.24	174	trace
17	diphenylmethane	77.94	168	trace
18	1,1'-(1-methyl-1,2-ethanediyl)bisbenzene	81.57	196	0.28
19	dibenzyl	82.29	182	1.11
20	1,1'-ethenyldienebisbenzene	82.64	180	0.32
21	1,1'-(1-butene-1,4-diyl)bisbenzene	86.99	208	0.47
22	2-phenyl-2,3-dihydroindene	88.39	194	trace
23	1,1'-(1,3-propandiyl)bisbenzene	89.18	196	0.85
24	1,1'-[1-(2-propenyl)-1,2-ethanediyl]bisbenzene	89.41	222	0.25
25	1,3-dimethyl-3-butenylbenzene	92.06	160	0.55
26	(3-phenylbut-3-enyl)benzene or styrene dimer	94.32	208	20.21

TABLE 6.2.4 (continued). Compounds identified in the pyrogram of poly(styrene-co-divinylbenzene) 2% crosslinked, shown in Figure 6.2.4.

Peak	Compound	Ret. Time	MW	Area %
27	1,1'-(2-pentene-1,5-diyl)bisbenzene	94.45	222	0.18
28	1,1'-(2-butene-1,4-diyl)bisbenzene	96.12	208	0.27
29	1,1'-cyclopropylidenebisbenzene	98.52	194	0.87
30	1-(4-methylphenyl)-4-phenylbuta-1,3-diene	98.87	220	0.96
31	2,5-diphenyl-pent-1-ene	99.16	222	0.22
32	(?-phenylhex-?-enyl)benzene	99.70	236	0.50
33	1,1'-(1,2-ethenediyl)bis-benzene	100.18	180	0.98
34	1,1'-(1-hexene-1,4-diyl)bisbenzene	101.96	236	1.80
35	2,5-diphenyl-1,5-hexadiene	103.29	234	2.50
36	1,4-diphenyl-1,3-butadiene	104.03	206	0.67
37	1,5-diphenyl-1,5-hexadiene	105.79	234	0.36
38	1,2-diphenylcyclohexene ?	106.24	234	0.59
39	1,2-diphenylcyclohex-?-ene ?	107.18	234	1.23
40	1-(4-ethylphenyl)-4-phenylbuta-1,3-diene	108.61	236	0.42
41	1,1'-(1,5-hexadiene-1,6-diyl)bisbenzene	109.68	234	0.54
42	1,6-diphenyl-1,5-hexadiene	114.69	234	1.38
43	tricyclo[9.2.2.2(4,7)heptadeca-1(14),2,4(17),5,7(16)-11(15),-12-heptaene ?	115.64	220	0.96

The comparison of the pyrograms and the corresponding list of compounds in the pyrolysate for poly(styrene-co-divinylbenzene) 2% cross-linked and for polystyrene indicates that the copolymer generates less monomer (48.5% vs. 55.2%) and less dimer (20.2% vs. 23.7%). Also, the comparison of the two pyrograms shows that the copolymer has a more complex pyrogram. Compounds such as 4-ethyl-1-ethenylbenzene (3.0%) or 1,4-divinylbenzene (2.2%) were expected in the pyrolysate of the copolymer, and they are the result of cleavage of 1,4-divinylbenzene units from the copolymer chain. Some other peaks present at trace level and not detected in polystyrene were noticeable in the copolymer. This indicates that crosslinking affects in general the pyrolysis process, and a less uniform polymer is likely to be generated upon crosslinking, with a more complex pyrolysate. Other studies on pyrolysis of this copolymer were reported in literature [108–110], etc.

Another example of a pyrogram is given in Figure 6.2.5 for poly(styrene-co-acrylonitrile), 25 wt % acrylonitrile, CAS# 9003-54-7, with $M_w = 165,000$. The idealized structure of the copolymer is $[-CH_2CH(C_6H_5)-]_x[-CH_2CH(CN)-]_y$. The pyrolysis was done at 600° C in He with separation of a Carbowax column and MS detection, similarly to other polymers discussed in this book (see also Table 4.2.2). The peak identification for the chromatogram shown in Figure 6.2.5 was done using MS spectral library searches only and is given in Table 6.2.5.

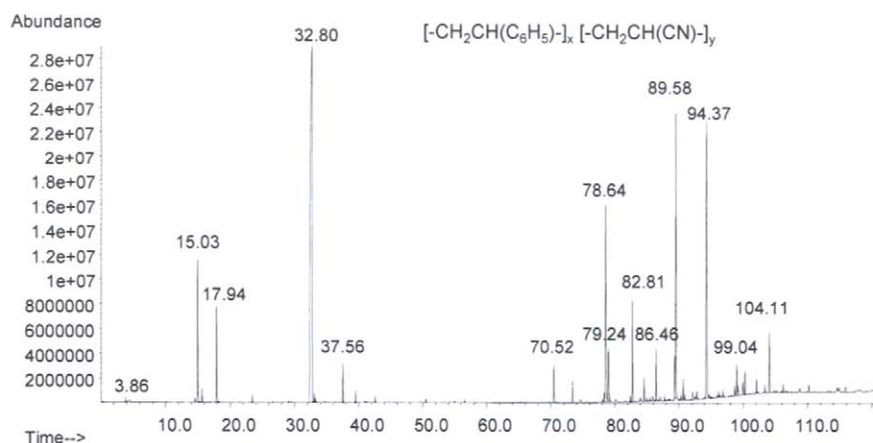


FIGURE 6.2.5. Result for a Py-GC/MS analysis of poly(styrene-co-acrylonitrile) 25% wt. acrylonitrile, $M_w = 165,000$. Pyrolysis done at 600°C in He, with the separation on a Carbowax type column.

TABLE 6.2.5. Compounds identified in the pyrogram of poly(styrene-co-acrylonitrile) 25% wt. acrylonitrile, $M_w = 165,000$, as shown in Figure 6.2.5.

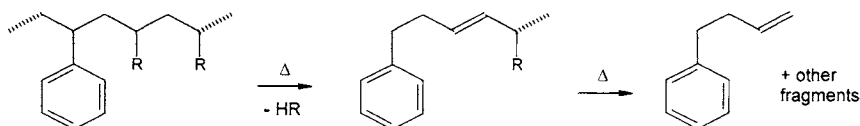
Peak	Compound	Ret. Time	MW	Area %
1	benzene	12.64	78	trace
2	2-propenenitrile (acrylonitrile)	15.03	53	5.47
3	acetonitrile	15.67	41	0.36
	hydrocyanic acid	16.63	27	trace
4	propanenitrile	17.17	55	trace
5	toluene	17.94	92	2.85
6	1-cyano-2-butene	18.89	81	trace
7	ethylbenzene	23.49	106	0.22
8	isopropylbenzene	26.63	120	trace
9	propylbenzene	29.13	120	trace
10	2-methylenepent-4-enenitrile	29.54	93	trace
11	styrene	32.80	104	39.39
12	1-propenylbenzene	33.10	118	0.20
13	4-cyano-1-butene	33.31	81	trace
14	α -methylstyrene	37.56	118	1.03
15	3-butenylbenzene	39.55	132	0.33
16	(1-methylenepropyl)benzene	40.99	132	trace
17	(1-methylene-2-propenyl)benzene	41.16	130	trace
18	2-propenylbenzene	42.56	118	0.16
19	acetic acid	45.43	60	trace
20	2-pentenylbenzene	46.68	146	trace
21	indene	47.99	118	trace
22	1,4-dihydronaphthalene	49.56	130	trace
23	1-cyclopent-1-yl-benzene	50.49	144	trace
24	2-phenyl-1-hexene	51.93	160	trace
25	2-ethyl-1H-indene	54.23	144	trace
26	1-phenyl-cyclohex-1-ene	54.84	158	trace

TABLE 6.2.5 (continued). Compounds identified in the pyrogram of poly(styrene-co-acrylonitrile) 25% wt. acrylonitrile, $M_w = 165,000$, as shown in Figure 6.2.5.

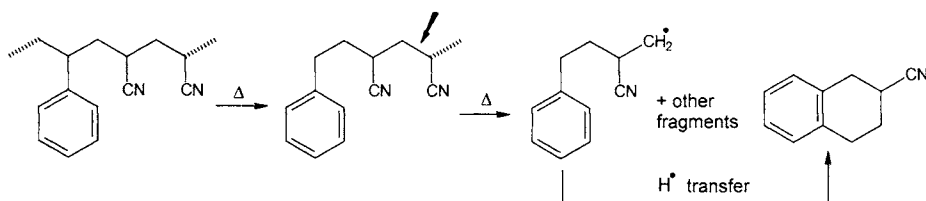
Peak	Compound	Ret. Time	MW	Area %
27	1,2-dihydronaphthalene	56.56	130	trace
28	2-cyclopent-1-yl-benzene	64.19	144	trace
29	3-phenyl-2-propenenitrile	70.52	129	1.15
30	benzyl nitrile	73.43	117	0.67
31	(1-methyl-3-butenyl)-benzene	78.35	146	0.33
32	2-(2-phenylethyl)prop-2-enenitrile	78.64	157	8.97
33	2-methylenepentanedinitrile	79.04	106	1.81
34	α -methylbenzeneacetonitrile	79.16	131	0.21
35	bibenzyl	82.44	182	0.19
36	benzenebutanenitrile	82.81	145	3.05
37	propane-1,3-dicarbonitrile (pentanedinitrile)	84.45	94	trace
38	α -methylenebenzeneacetonitrile	84.59	129	0.73
39	N-phenylbenzenamine	86.46	169	1.47
40	1,1'-(1,3-propandiy)bisbenzene	89.34	196	1.27
41	4-phenylpent-4-enenitrile	89.58	157	10.48
42	2-(2-phenylethyl)pent-2-enenitrile	90.69	185	0.64
43	2,4-diphenyl-1-pentene	92.19	222	0.36
44	1,2,3,4-tetrahydronaphthalene-2-carbonitrile	92.85	157	0.32
45	(3-phenylbut-3-enyl)benzene or styrene dimer	94.37	208	10.99
46	2-naphthalenecarbonitrile	96.23	153	0.23
47	3-(phenylmethyl)pyridine	96.87	169	0.23
48	1,1'-cyclopropylidenebisbenzene	98.69	194	0.35
49	1-(4-methylphenyl)-4-phenylbuta-1,3-diene	99.04	220	1.12
50	2,5-diphenyl-pent-1-ene	99.25	222	0.38
51	?-methyl-?-phenylhexanenitrile	100.00	185	0.64
52	1,1'-(1,2-ethenediy)bis-benzene	100.34	180	0.72
53	1,1'-(?-butene-1,4-diyl)bisbenzene	102.11	208	0.45
54	2,5-diphenyl-1,5-hexadiene	103.43	234	0.26
55	1,1'-(?-hexene-1,4-diyl)bisbenzene	104.11	236	2.03
56	2-(phenylmethyl)pyridine	106.26	169	0.30
57	?-(?-cyanobutenyl)benzenecarbonitrile	110.24	182	0.34
58	tricyclo[9.2.2.2(4,7)heptadeca-1(14),2,4(17),5,7(16)-11(15),-12-heptaene ?	115.91	220	0.29

The elimination of HCN from the side chain of the polymer generates double bonds in the backbone, which accelerates further decomposition due to the cleavage of the backbone in the β -position to the double bond. Both styrene (A) and acrylonitrile (B) are formed in the pyrolysate in relatively large amounts, allowing an immediate identification of this copolymer as poly(styrene-co-acrylonitrile). Compounds such as benzene-butanenitrile (3.1%) or α -methylene-benzeneacetonitrile (0.7%) also are generated from the copolymer indicating segments of AB type, and therefore a likely random structure of the polymer. Since dimers of AA and BB type are also generated in considerable proportions (about 11% for distyrene and about 1.8% for 2-methylenepentanedinitrile), this shows that the polymer is not of alternating type and confirms the random nature.

Among other types of fragments detected in the pyrolysis of poly(styrene-co-acrylonitrile) are compounds such as 3-butenylbenzene, 2-pentenylbenzene, 2-phenyl-1-hexene. These compounds are likely generated in reactions as shown for 3-butenylbenzene:



where R can be either CN or phenyl. Both HCN and benzene are seen in the pyrolysate, although fragment molecules with a long alkyl side chain are less common in polystyrene pyrolysate. This would suggest that R is more frequently CN. Other compounds are generated in reactions following the chain fragmentation. For example, 1,2,3,4-tetrahydronaphthalene-2-carbonitrile is probably generated in a reaction as shown below:



The variety of possible reactions during the pyrolysis of this copolymer explains the added complexity of the pyrolysate, as compared to that of individual homopolymers (see also [111, 112]).

Pyrolysis results for a sample of poly(styrene-co-methyl methacrylate) 40% styrene, CAS# 25034-86-0, are shown in Figure 6.2.6. The $M_w \approx 100,000$ -150,000 and the idealized structure of the sample is $[-CH_2CH(C_6H_5)-]_x[-CH_2C(CH_3)(COOCH_3)-]_y$. The pyrolysis was done at 600° C in He with separation of a Carbowax column and MS detection, similarly to other polymers discussed in this book (see also Table 4.2.2). The peak identification for the chromatogram shown in Figure 6.2.6 was done using MS spectral library searches only and is given in Table 6.2.6.

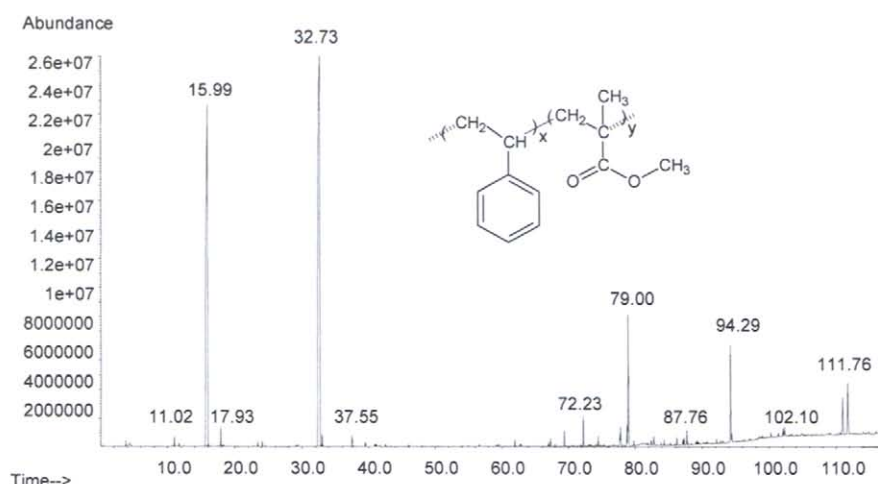


FIGURE 6.2.6. Result for a Py-GC/MS analysis of poly(styrene-co-methyl methacrylate) 40% wt. styrene, $M_w = 100,000$ – $150,000$. Pyrolysis done at 600°C in He, with the separation on a Carbowax type column.

TABLE 6.2.6. Compounds identified in the pyrogram of poly(styrene-co-methyl methacrylate) 40% wt. styrene, $M_w = 100,000$ – $150,000$, as shown in Figure 6.2.6.

Peak	Compound	Ret. Time	MW	Area %
1	carbon dioxide	4.40	44	0.09
2	2-methylpropene	4.55	56	trace
3	methanol	10.73	32	trace
4	propanoic acid methyl ester	11.02	88	0.30
5	2-methylpropanoic acid methyl ester	11.72	102	trace
6	2-propenoic acid methyl ester	12.43	86	trace
7	2-methyl-2-propenoic acid methyl ester (monomer B)	15.99	100	31.83
8	toluene	17.93	92	0.56
9	ethylbenzene	23.49	106	trace
10	4-methyl-4-pentenoic acid methyl ester	24.11	128	trace
11	2,4-dimethyl-4-pentenoic acid methyl ester	29.39	142	trace
12	styrene	32.73	104	46.32
13	1-propenylbenzene	33.07	118	1.83
14	α -methylstyrene	37.55	118	0.36
15	3-butenylbenzene	39.55	132	trace
16	(1-methylenepropyl)benzene	40.99	132	trace
17	2-propenylbenzene	42.56	118	trace
18	2-pentenylbenzene	46.68	146	trace
19	2,4-pentandioic acid dimethylester	56.63	188	trace
20	2-pentenedioic acid dimethyl ester	59.55	158	trace
21	1,2-dimethyl-1,2-dicarboxymethylcyclopropane	61.99	186	0.22
22	(1-methylbuta-1,3-dienyl)benzene	62.78	144	trace
23	4-ethyl-2-methylenepentanedioic acid dimethyl ester	62.91	200	trace
24	α -methylbenzenepropanoic acid methyl ester	67.03	178	trace
25	4-methyl-2-pentenoic acid	67.31	114	0.32
26	2-methyl-5-methylenhexandioic acid dimethyl ester	69.39	200	0.52

TABLE 6.2.6 (continued). Compounds identified in the pyrogram of poly(styrene-co-methyl methacrylate) 40% wt. styrene, $M_w = 100,000\text{--}150,000$, from Figure 6.2.6.

Peak	Compound	Ret. Time	MW	Area %
27	α -methylenebenzenepropanoic acid methyl ester	72.23	176	1.00
28	2-methyl-4-phenylbutyric acid methyl ester	74.46	192	0.33
29	2-methylene-4-phenylbutyric acid methyl ester	77.70	190	0.38
30	2-[4-(1-buten-3-yl)phenyl]propanoic acid methyl ester	77.83	218	0.65
31	6-phenyl-6-heptenoic acid methyl ester	78.80	218	0.70
32	methyl 2-methyl-1,2,3,4-tetrahydronaphthalene-2-carboxylate	79.00	204	4.36
33	1,1'-ethenyldienebisbenzene	82.81	180	0.40
34	$C_{17}H_{14}$	86.26	218	0.32
35	1,1'-(1-butene-1,4-diyl)bisbenzene	86.99	208	trace
36	7-phenyl-5-hepten-2-one ?	87.32	188	0.26
37	unknown [117(100), 115(28), 204(21), 144(19), 129(16)]	87.76		0.47
38	(3-phenylbut-3-enyl)benzene or styrene dimer	94.29	208	3.38
39	1,1'-(2-pentene-1,5-diyl)bisbenzene	94.46	222	0.30
40	1,1'-(1,2-ethenediyl)bis-benzene	100.18	180	trace
41	1,1'-(2-butene-1,4-diyl)bisbenzene	102.10	208	0.25
42	unknown	102.34		0.34
43	2,4-dimethyl-4-(2-phenylprop-2-enyl)-1,5-pentanedioic acid dimethyl ester ?	111.03	304	1.91
44	?,?-dimethyl-4-(2-phenylprop-2-enyl)-1,5-pentanedioic acid dimethyl ester ?	111.76	304	2.58

The pyrolysis results for poly(styrene-co-methyl methacrylate) are very similar to those for poly(styrene-co-acrylonitrile). The monomer of both comonomers (A styrene, B methyl methacrylate) are seen in the pyrolysate. Also, fragments resulting from two styrene or from two methyl methacrylate units are seen. In addition, a fragment molecule was tentatively assigned as AB type for the peak eluting at 79.0 min. The spectrum of this peak is shown in Figure 6.2.7. Tentative structures of some fragments are also shown together with the spectrum. No similar spectra were available in common mass spectral libraries.

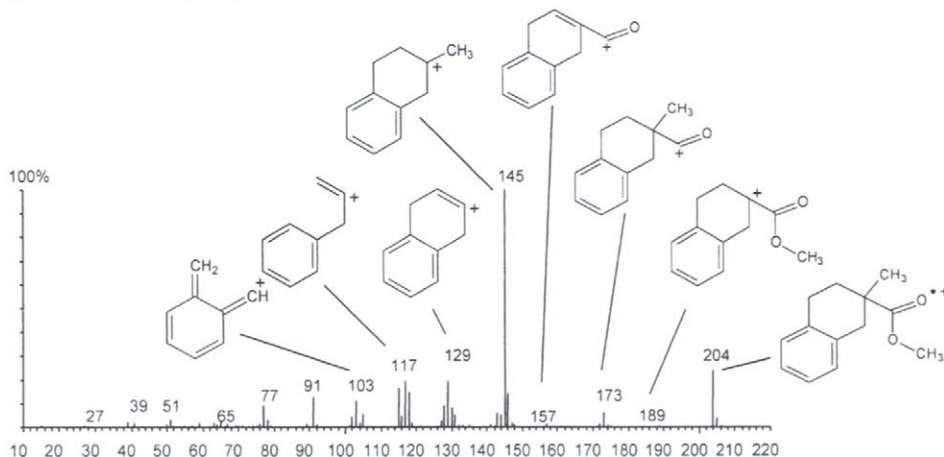
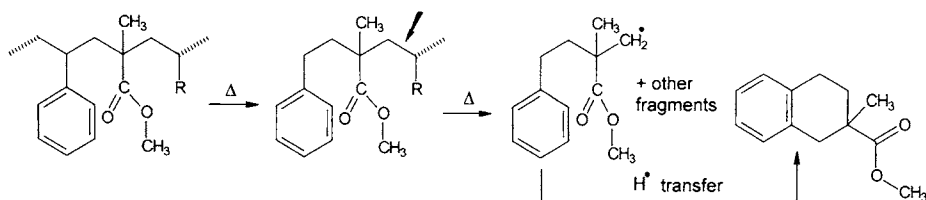


FIGURE 6.2.7. Tentatively assigned spectrum for methyl 2-methyl-1,2,3,4-tetrahydronaphthalene-2-carboxylate MW = 204 (ret. time 79.0 min.).

The formation of methyl 2-methyl-1,2,3,4-tetrahydro-naphthalene-2-carboxylate can be explained by reactions similar to that of 1,2,3,4-tetrahydronaphthalene-2-carbonitrile from the pyrolysis of poly(styrene-co-acrylonitrile), and it is shown below:



Tentatively identified in the pyrogram are also two fragments of the type ABB, eluting at 111.03 min., and 111.76 min.

Among the copolymers of styrene that have practical applications is poly(styrene-co-maleic anhydride) [71]. The pyrogram of a sample of poly(styrene-co-maleic anhydride), CAS# 9011-13-6, with 7% wt. maleic anhydride and $M_w = 224,000$ is given in Figure 6.2.8. The pyrolysis was done at 600°C in He with separation of a Carbowax column and MS detection, similarly to other polymers discussed in this book (see Table 4.2.2).

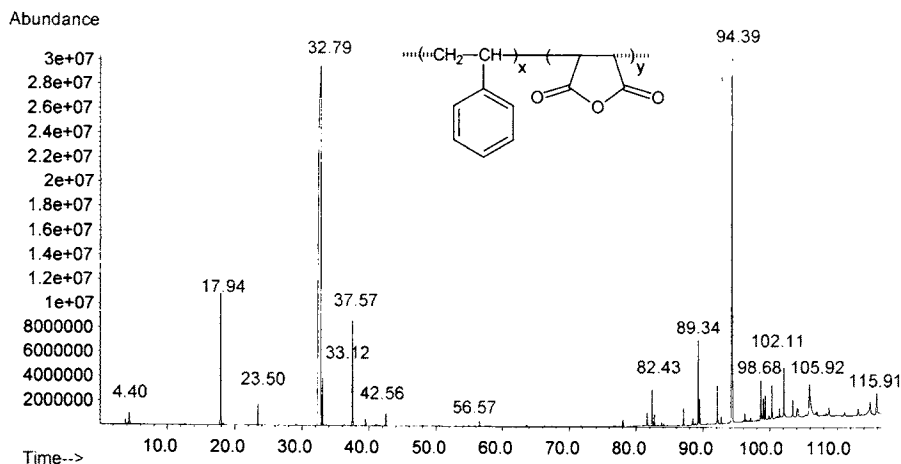


FIGURE 6.2.8. Result for a Py-GC/MS analysis of poly(styrene-co-maleic anhydride) 7% wt. maleic anhydride, $M_w = 224,000$. Pyrolysis done at 600°C in He, with the separation on a Carbowax type column.

The pyrogram shown in Figure 6.2.8 is almost identical to that given in Figure 6.2.2 for polystyrene. The only additional peak compared to polystyrene pyrolysate elutes at 105.92 min. and has the spectrum shown in Figure 6.2.9. This spectrum was tentatively assigned to 3-(1-phenylvinyl)-3,4-dihydrofuran-2,5-dione (MW = 202), which is the AB type fragment for this copolymer. Some ions detected in the mass spectrum are shown with their likely structure.

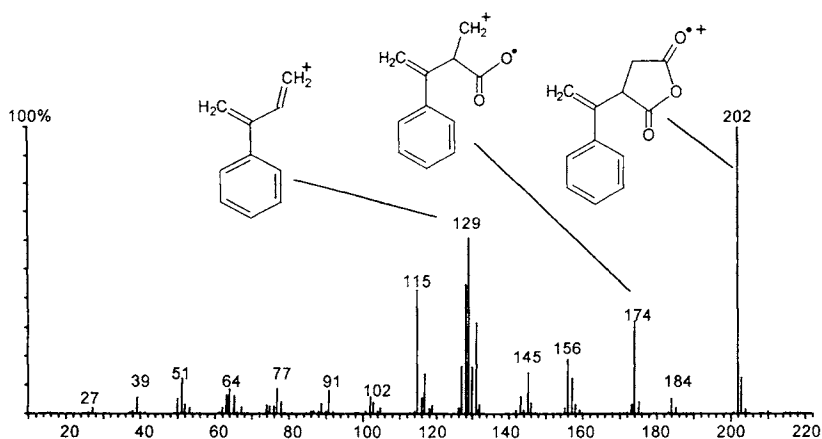


FIGURE 6.2.9. Mass spectrum tentatively assigned to 3-(1-phenylvinyl)-3,4-dihydrofuran-2,5-dione.

The assignment of spectrum given in Figure 6.2.9 was not verified with that of other similar compounds since no compound with a similar enough structure was found in common mass spectral libraries.

A variety of styrene-butadiene copolymers are used in practice. The results for the pyrolysis of a polystyrene-*block*-polybutadiene sample 30 wt % styrene, 80% diblock (with added BHT as antioxidant) and CAS# 9003-55-8 are shown in Figure 6.2.10. The pyrolysis was done similarly to other polymers discussed in this book (see Table 4.2.2).

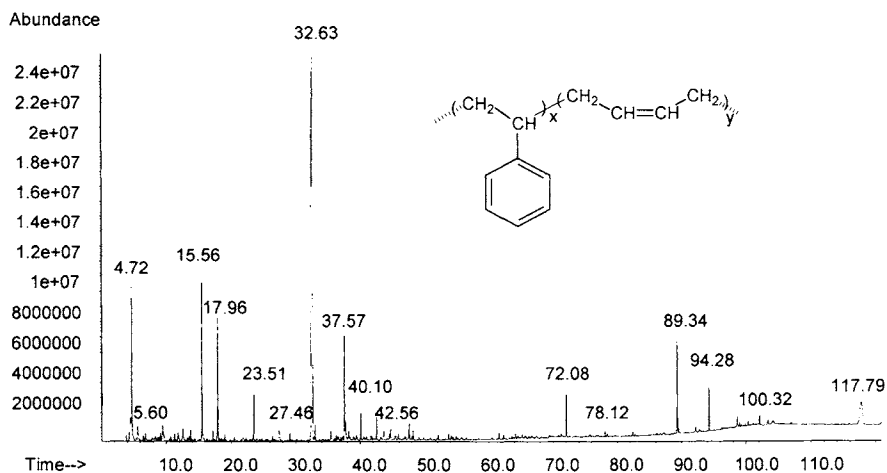


FIGURE 6.2.10. Result for a Py-GC/MS analysis of polystyrene-*block*-polybutadiene 30 wt % styrene, 80% diblock. Pyrolysis done at 600° C in He, with the separation on a Carbowax type column.

The peak identification for the chromatogram shown in Figure 6.2.10 was done using MS spectral library searches only and is given in Table 6.2.7.

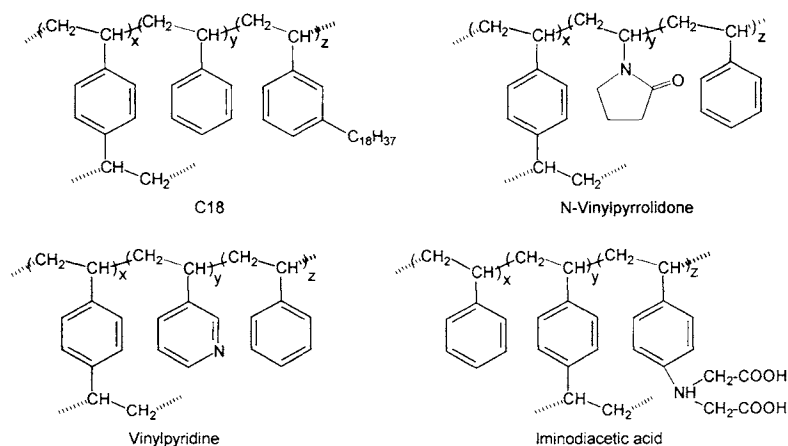
TABLE 6.2.7. Compounds identified in the pyrogram of polystyrene-block-polybutadiene 30 wt % styrene, 80% diblock, as shown in Figure 6.2.10.

Peak	Mono.*	Compound	Ret. Time	MW	Area %
1	B	ethane	3.86	30	trace
2	B	1-propene	4.43	42	0.58
3	B	2-methylpropene	4.55	56	0.70
4	B	2-butene	4.62	56	0.82
5	B	1,3-butadiene	4.72	54	5.54
6	B	1,3-pentadiene	5.60	68	0.87
7	B	1,4-pentadiene	5.75	68	0.41
8	B	1,4-hexadiene	6.89	82	0.69
9	B	cyclohexene	9.27	82	0.26
10	B	1,3,5-hexatriene	9.50	80	0.62
11	B	(?,?)-1,3,6-octatriene	11.28	108	0.23
12	B	?,?-octadiene	11.34	110	0.31
13	B	2,6-octadiene	11.88	110	0.68
14	B,S	benzene	12.63	78	0.98
15	B	ethenylcyclohexane	13.76	110	0.46
16	B	4-ethenylcyclohex-1-ene	15.56	108	7.11
17	B	1,2-dimethylenecyclohexene	15.69	108	0.28
18	B	(Z,E)-1,3,5-octatriene	17.25	108	0.34
19	B,S	toluene	17.96	92	6.33
20	B	2,3-dimethyl-1,3-cyclohexadiene	19.09	108	0.29
21	B,S	ethylbenzene	23.51	106	2.26
22	B,S	1,4-dimethylbenzene	27.46	106	0.66
23	B	propylbenzene	29.12	120	0.32
24	B,S	styrene	32.63	104	40.29
25	S	1-propenylbenzene	33.04	118	0.67
26	B	4-methylene-tricyclo[5,2,1,0E2,6]decane	35.49	148	0.53
27	S	1-vinyl-4-methylbenzene	37.57	118	4.69
28	B	1,5-diethenyl-3-methyl-2-methylenecyclohexane	37.74	162	0.82
29	B	1,4-divinyl-octahydropentalene	38.19	162	0.35
30	B	spiro[2.9]dodeca-4,8-diene ?	40.10	162	1.20
31	S	2-propenylbenzene	42.56	118	0.92
32	B	spiro[2.9]dodeca-5,9-diene ?	43.71	162	0.46
33	B	2,6-diethenyl-cis-cyclooctene ?	44.75	162	0.51
34	?	1-methylenebutylbenzene	45.93	146	0.42
35	B	2,6-diethenyl-cis-cyclooctene isomer	47.66	162	1.41
36	B	spiro[2.9]dodeca-4,8-diene isomer	48.24	162	0.62
37	B	(E,E,E)-1,4,8-dodecatriene	52.16	162	0.35
38	S	1,3-divinylbenzene	53.78	130	0.28
39	?	1-phenyl-1,3-heptadiene	61.63	172	0.38
40	?	4-methyl-2,6-(1,1-dimethylethyl)phenol (BHT)	72.08	220	1.96
41	S	diphenylmethane	78.12	168	0.31
42	S	1,1'-(1,3-propandiyl)bisbenzene	89.34	196	4.10
43	S	(3-phenylbut-3-enyl)benzene or styrene dimer	94.28	208	2.33
44	S	1,1'-cyclopropylidenebisbenzene	98.68	194	0.60
45	S	1,1'-(1,2-ethenediyl)bis-benzene	100.32	180	0.30
46	?	1,1'-(1-butene-1,4-diyl)bisbenzene	102.10	208	0.59
47	?	unknown [91(100), 117(32), 207(21), 194(17)...312(4)]	117.71	312	5.13

* Letter B designates compounds originated from butadiene monomer and letter S designates those originated from styrene. B,S indicates that both homopolymers generate the fragment.

The pyrogram of this block copolymer is, as expected, almost identical to the superposition of the pyrograms of the individual homopolymers butadiene and styrene. Some compounds such as benzene, toluene, styrene, etc. are indicated as B,S because they are generated from both copolymers, although not necessarily in the same proportion. They are not AB type compounds. The origin of a few compounds is not clear. Probably very low levels of AB type compounds are still present in the pyrogram, but they are below the detection capability of the instrumentation.

Polystyrene alone, or polystyrene having different degrees of crosslinking with divinylbenzene is commonly used in numerous copolymers with special purposes. Polymers used as stationary phases in chromatography may include groups such as C18 chains, pyridine, N-vinylpyrrolidone, or iminodiacetic acid groups. The structures of such copolymers are indicated below:



Pyrolysis results for a sample of poly(2-vinylpyridine-co-styrene) 30% styrene, CAS# 24980-54-9, are shown in Figure 6.2.11. The $M_w \approx 220,000$ and the idealized structure of the sample is $[-CH_2CH(2-C_5H_4N)-]_x [-CH_2CH(C_6H_5)-]_y$. The pyrolysis was done at $600^\circ C$ in He with separation of a Carbowax column and MS detection, similarly to other polymers discussed in this book (see also Table 4.2.2). The peak identification for the chromatogram shown in Figure 6.2.11 was done using MS spectral library searches only and is given in Table 6.2.8.

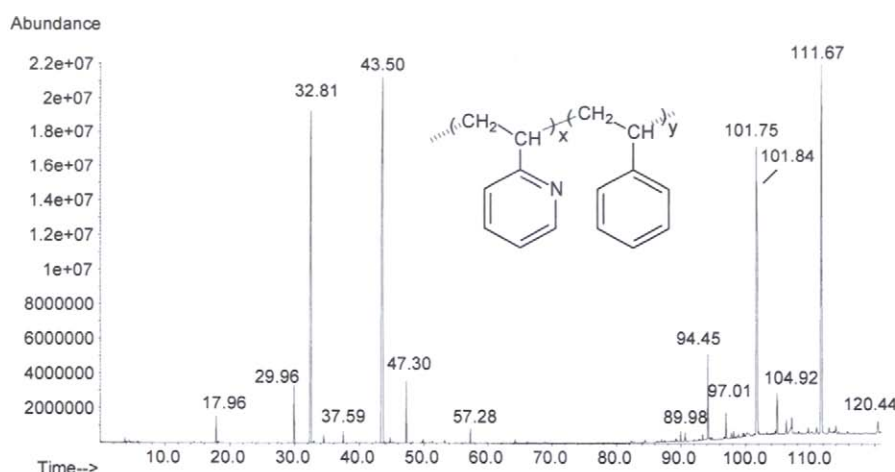


FIGURE 6.2.11. Result for a Py-GC/MS analysis of poly(2-vinylpyridine-co-styrene) 30% styrene, $M_w \approx 220,000$. Pyrolysis done at 600°C in He, with the separation on a Carbowax type column.

TABLE 6.2.8. Compounds identified in the pyrogram of poly(2-vinylpyridine-co-styrene) 30% styrene, $M_w \approx 220,000$, as shown in Figure 6.2.11.

Peak	Compound	Ret. time	MW	Area %
1	toluene	17.96	92	0.75
2	2-methylpyridine	29.96	94	1.67
3	ethenyl benzene (styrene)	32.81	104	20.43
4	2-ethylpyridine	34.47	106	trace
5	α -methylstyrene	37.59	118	0.31
6	2-ethenylpyridine (monomer)	43.50	105	28.58
7	2,3-dihydro-1H-indole	47.30	119	1.73
8	1,2,3,4-tetrahydroquinoline	49.90	133	trace
9	2,3-cyclopentenopyridine	50.92	119	trace
10	5,6,7,8-tetrahydroquinoline	51.35	133	trace
11	2,3-dihydro-1H-isoindole	57.28	119	0.42
12	indolizine	64.20	117	trace
13	3-methylindolizine	66.15	131	trace
14	2-methylindole	68.92	131	trace
15	2-(2-phenylethyl)-pyridine	90.66	183	0.31
16	(3-phenylbut-3-enyl)benzene or styrene dimer	94.45	208	2.60
17	2-N-(3'-phenylpropyl)pyridine	97.01	197	0.76
18	2-(3-phenylbut-3-enyl)pyridine	101.75	209	10.60
19	2-[1-(2-phenylethyl)vinyl]pyridine	101.84	209	6.12
20	2,2'-(1,3-propandiy)bis-pyridine	104.92	198	1.41
21	2-[1-[2-(2-pyridyl)propyl]vinyl]pyridine	106.34	224	0.49
22	(1-methylene-3-phenylbut-3-enyl)benzene	107.17	220	1.07
23	2-[3-(2-pyridyl)but-1-enyl]pyridine (vinylpyridine dimer)	111.67	210	22.09
24	2-[1-methylene-3-(2-pyridyl)but-1-enyl]pyridine	120.44	222	0.67

The pyrogram of poly(2-vinylpyridine-co-styrene) is typical for a random copolymer. Both styrene and 2-vinylpyridine monomers as well as their dimers are present in the pyrogram (see also Section 6.5 for pyrolysis of poly(2-vinylpyridine)). In addition, AB types compounds are seen in the pyrogram. The spectra of 2-(3-phenylbut-3-enyl)pyridine and of 2-[1-(2-phenylethyl)vinyl]pyridine are shown in Figure 6.2.12 and 6.2.13. These spectra are not available in common mass spectral libraries (Nist 98, Wiley 275, etc.).

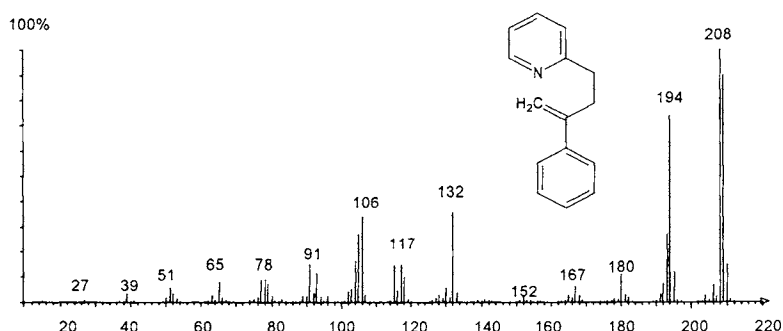


FIGURE 6.2.12. Mass spectrum assigned to 2-(3-phenylbut-3-enyl)pyridine.

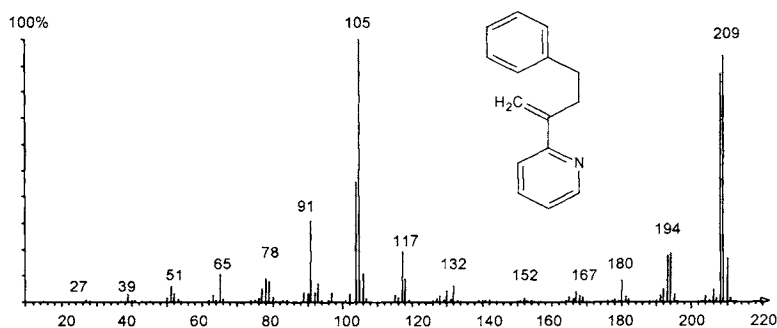


FIGURE 6.2.13. Mass spectrum assigned to 2-[1-(2-phenylethyl)vinyl]pyridine.

It is very likely that the pyrolysis of poly(2-vinylpyridine-co-styrene) takes place by a random scission mechanism characteristic for both styrene and poly(2-vinylpyridine). Both benzene and pyridine were detectable in the pyrogram, but their levels were extremely low and these compounds are not included in Table 6.2.8 (even as trace type compounds). The presence of benzene and pyridine may be the result of the elimination of these compounds at very low level from the polymer backbone, but more likely they are formed from the free radicals that are already generated from the backbone cleavage.

Pyrolysis results for a sample of poly(1-vinylpyrrolidone-co-styrene), CAS# 25086-29-7, are shown in Figure 6.2.14. The pyrolysis was done at 600° C in He with separation on a Carbowax column and MS detection, similarly to other polymers discussed in this book (see also Table 4.2.2). The peak identification for the chromatogram shown in Figure 6.2.14 was done using MS spectral library searches only and is given in Table 6.2.9.

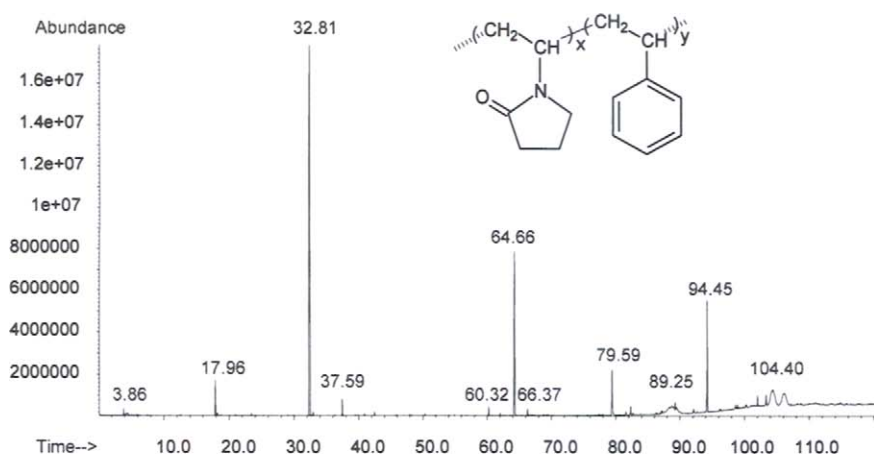


FIGURE 6.2.14. Result for a Py-GC/MS analysis of poly(1-vinylpyrrolidone-co-styrene). Pyrolysis done at 600° C in He, with the separation on a Carbowax type column.

TABLE 6.2.9. Compounds identified in the pyrogram of poly(1-vinylpyrrolidone-co-styrene), as shown in Figure 6.2.14.

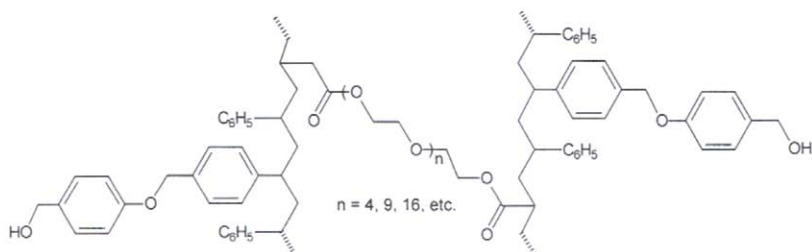
Peak	Compound	Ret. time	MW	Area %
1	formaldehyde	5.08	30	trace
2	acetaldehyde	5.96	44	trace
3	benzene	12.62	78	trace
4	toluene	17.96	92	2.99
5	water	18.25	18	trace
6	ethylbenzene	23.41	106	trace
7	propylbenzene	29.05	120	trace
8	ethenyl benzene (styrene)	32.81	104	53.82
9	α -methylstyrene	37.59	118	1.29
10	3-butenylbenzene	39.41	132	trace
11	phenyl-1-butene	40.91	132	trace
12	2-propenylbenzene	42.42	118	trace
13	indene	47.99	118	trace
14	benzaldehyde	50.30	106	trace
15	1-methyl-2-pyrrolidinone	60.32	99	0.76
16	1-ethyl-2-pyrrolidinone	62.11	113	trace
17	1-ethenyl-2-pyrrolidinone (monomer)	64.66	111	18.39
18	1-(methylethyl)-2-pyrrolidin-5-one	66.37	125	0.69
19	2-pyrrolidinone	79.59	85	5.55
20	1,1'-(1-methyl-1,2-ethanediyl)bisbenzene	81.57	196	trace
21	bibenzyl	82.36	182	0.89

TABLE 6.2.9 (continued). Compounds identified in the pyrogram of poly(1-vinylpyrrolidone-co-styrene), as shown in Figure 6.2.14.

Peak	Compound	Ret. time	MW	Area %
22	?, ?, ?-trimethylcarbazole ?	88.75	209	0.74
23	1,1'-(1,3-propanediyl)bisbenzene	89.25	196	0.75
24	2,4-diphenyl-1-pentene	92.12	222	trace
25	(3-phenylbut-3-enyl)benzene or styrene dimer	94.45	208	9.42
26	1,1'-(2-butene-1,4-diyl)bisbenzene	96.12	208	trace
27	1,1'-cyclopropyldienebisbenzene	98.60	194	0.49
28	1-(4-methylphenyl)-4-phenylbuta-1,3-diene	98.94	220	0.37
29	1,1'-(1,2-ethenediyl)bis-benzene	100.25	180	0.75
30	1,1'-(1-butene-1,4-diyl)bisbenzene	102.03	208	2.01
31	2,5-diphenyl-1,5-hexadiene	103.35	234	1.09
32	unknown impurity	104.40		not incl.
33	unknown impurity	106.60		not incl.

The pyrogram of poly(1-vinylpyrrolidone-co-styrene) shows several compounds resulting from the styrene sequences and also the monomer and some related molecules for vinylpyrrolidone sequences (see also Section 6.5). However, the dimer 1-[3-(2-oxopyrrolidinyl)but-3-enyl]pyrrolidin-2-one and AB type compounds were not detected in the pyrolysate, possibly due to the selection of the chromatographic column that does not elute easily polar compounds.

One of many applications of polystyrene type resins is in solid phase peptide synthesis where special copolymers are used (Wang resins and Merrifield resins). Wang resins contain 4-benzyloxybenzyl alcohol groups bound to the polystyrene backbone. Some crosslinking is common in these resins, and divinylbenzene or ethylenedimethacrylate can be used for this purpose. In order to generate a flexible solid structure, the polystyrene chains also can be crosslinked with polyethyleneglycol diacrylate groups (see also Section 9.1). The resulting structure of the Wang resin has the idealized formula shown below:



The OH groups of the benzyl alcohol can be esterified with a carboxylic group, e.g. in the presence of diisopropylcarbodiimide (DIC). The carboxyl group can belong to any acid, but the procedure is typically used for amino acids. The amino function can be protected with a 9-fluorenylmethoxycarbonyl group (Fmoc). The resulting material is used in solid phase synthesis of peptides by repeatedly unprotecting the amino acid and adding a new amino acid to form a dipeptide (e.g. in the presence of BOC, EDAC, or other compounds able to facilitate peptide bond formation [45]), which is again

protected, washed, unprotected and extended, until the desired peptide is generated. At the final point, the ester group to the benzyl alcohol is hydrolyzed (e.g. with trifluoroacetic acid) [113].

The pyrolysis of the copolymers formed from several monomer types, some with functionalities, generates complex pyrograms [114]. Depending on the content of each monomer type, the presence of related pyrolysis products is more or less intense. As an example the pyrolysis result of a Wang resin crosslinked with poly(ethylene glycol)(16) and having 0.8–1.5 mmol/g 4-benzyloxybenzyl alcohol is shown in Figure 6.2.15 together with the pyrogram of polystyrene (polystyrene pyrogram already shown in Figure 6.2.2). The pyrolysis was done at 600° C in He with separation of a Carbowax column and MS detection, similarly to other polymers discussed in this book (see also Table 4.2.2).

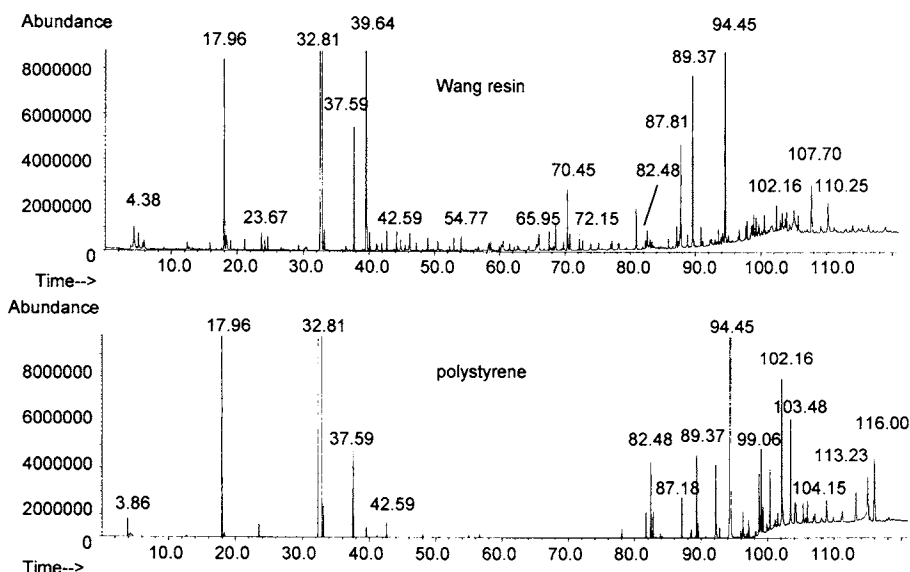
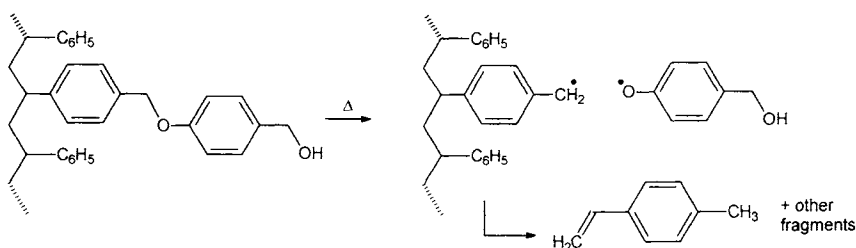


FIGURE 6.2.15. Result for a Py-GC/MS analysis of Wang polystyrene resin crosslinked with poly(ethylene glycol)(16) and having 0.8–1.5 mmol/g 4-benzyloxybenzyl alcohol (upper trace) and the pyrogram of polystyrene (lower trace). Pyrolysis done at 600° C in He, with the separation on a Carbowax type column.

Several major peaks are identical in the two traces shown in Figure 6.2.15. They are obviously generated from polystyrene sequences (segments), although different intensities are possible for the Wang resin compared to pure polystyrene. The peak at 39.64 min. belongs to 1-ethenyl-4-methyl-benzene and can be interpreted as resulting from the benzene fragments that initially belong to 4-benzyloxybenzyl alcohol groups. The cleavage of the C–O bond in 4-benzyloxybenzyl alcohol may leave methyl groups attached to the benzene ring in reactions as shown below:



However, the presence of some divinylbenzene in the resin may lead to the same compound, and the assignment cannot be done with certainty. Other compounds related to 4-benzyloxybenzyl alcohol and found in the pyrolysate include benzaldehyde (ret. time 50.56 min.) 4-methylbenzaldehyde (ret. time 58.30 min.), benzyl alcohol (ret. time 70.80 min.), 4-methylphenol (ret. time 80.97 min.), etc.

Other peaks from the Wang resin are generated from the poly(ethylene glycol) methacrylate bridges. Pyrolysis of poly(ethylene glycol) dimethacrylate by itself is discussed in Section 9.1. Figure 6.2.16 shows a portion of the pyrogram of the Wang resin (retention times between 40.0 min. and 90.0 min.) and the corresponding part from poly(ethylene glycol) dimethacrylate (as shown in Figure 9.1.8).

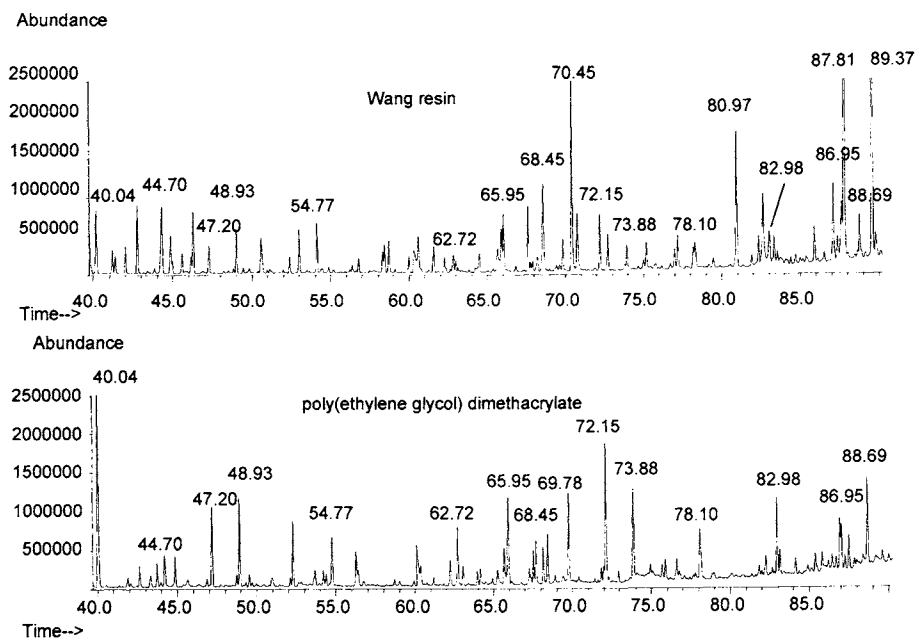


FIGURE 6.2.16. Time window between 40.0 min. and 90.0 min. from the pyrogram of a Wang resin (as shown in Figure 6.2.15) (upper trace) and the corresponding section from the pyrogram of poly(ethylene glycol) dimethacrylate (lower trace). Pyrolysis done at 600° C in He, with the separation on a Carbowax type column.

Most of the peaks shown in Figure 6.2.16 are ether type compounds or ester of 2-methyl-2-propenoic acid with fragments of poly(ethylene glycol). Some of these peaks were identified and given in Table 8.1.5 (see identical retention times). Besides the peaks resulting from the polystyrene and from poly(ethylene glycol) dimethacrylate, some compounds were fragments of the union groups. In conclusion, all groups from the resin are represented in the pyrolysate, and a detailed analysis allows the identification of each component part of the polymer. However, larger fragments from 4-benzyloxybenzyl alcohol such as phenylmethoxybenzene or substituted phenyl-methoxybenzenes were not detected in the pyrogram.

- *Poly(alkylstyrenes) and poly(arylstyrenes)*

Polymers derived from polystyrene but having alkyl or aryl groups substituted at the benzene ring were synthesized in an effort to improve some of polystyrene properties such as the impact resistance and obtain qualities similar to those achieved using copolymers with 1,3-butadiene (high impact polystyrene or HIPS). The polymers included in this class are poly(3-methylstyrene), poly(4-methylstyrene) CAS# 24936-41-2, poly(4-phenylstyrene) CAS# 25232-08-0 [115], as well as poly(2-vinylnaphthalene) CAS# 28406-56-6. Some of the reports regarding thermal decomposition of these polymers are summarized in Table 6.2.10.

TABLE 6.2.10. *Summary regarding reports on thermal decomposition of poly(alkylstyrene) and poly(arylstyrene).*

Polymer	Temp. °C	Results	Ref.
poly(3-methyl-styrene)	309–399	44.4% monomer, 7.3% xylene, 48.3% larger chain fragments	116
poly(4-methyl-styrene)	200–350	ratio of monomer to oligomer rises from 40% at 200° C to 95% at 350° C	117
poly(4-methyl-styrene)	560	C ₁ –C ₄ hydrocarbons, benzene, toluene, ethylbenzene, styrene, ethyltoluene, vinyltoluene, naphthalene, ethylstyrene	118, 119
poly(4-methyl-styrene)	500	small molecules resulting from random scission and β -scissions of the radicals.	119
poly(4-phenyl-styrene)	500	small molecules resulting from random scission and β -scissions of the radicals.	47

The results for a Py-GC/MS analysis of a sample of poly(vinyl toluene) (mixed isomers) CAS# 9017-21-4, $M_w = 80,000$ are shown in Figure 6.2.17. The pyrolysis was done from 0.4 mg material at 600° C in He at a heating rate of 20° C/ms with 10 s THT. The separation was done on a Carbowax column similar to other examples previously discussed (see Table 4.2.2). The peak identification for the chromatogram shown in Figure 6.2.17 was done using MS spectral library searches only and is given in Table 6.2.11. Some of the isomer positions are tentative only and reported in Table 6.2.11 as they resulted with the highest probability indicated by the mass spectral library search.

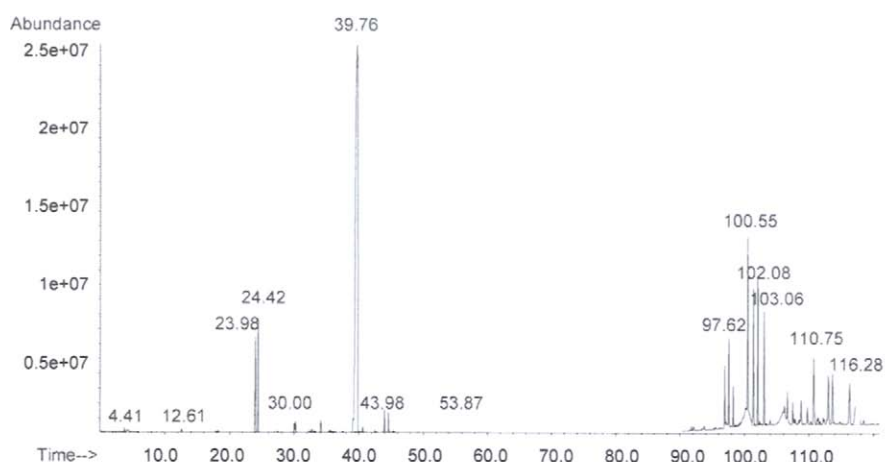


FIGURE 6.2.17. Result for a Py-GC/MS analysis of poly(vinyl toluene) (mixed isomers) $M_w = 80,000$. Pyrolysis done on 0.4 mg material at 600°C in He, with the separation on a Carbowax type column.

TABLE 6.2.11. Compounds identified in the pyrogram of poly(vinyl toluene) (mixed isomers) $M_w = 80,000$ shown in Figure 6.2.17.

Peak	Compound	Ret. Time	MW	Area %
1	2-methyl-1-propene	4.41	56	trace
2	benzene	12.61	78	trace
3	toluene	17.90	92	trace
4	water	18.25	18	trace
5	1,2-dimethylbenzene	23.98	106	2.50
6	1,4-dimethylbenzene	24.42	106	2.98
7	1-ethyl-4-methylbenzene	30.00	120	0.31
8	1-ethyl-3-methylbenzene	30.19	120	0.56
9	1,2,4-trimethylbenzene	34.12	120	0.31
10	1-ethenyl-3-methylbenzene	39.76	118	48.41
11	1-methyl-2-(2-propenyl)benzene	43.98	132	0.57
12	1-isopropenyl-4-methylbenzene	44.58	132	0.52
13	indene	47.95	116	trace
14	2-ethenyl-1,4-dimethylbenzene	49.20	132	0.33
15	1,3-diethenylbenzene	52.75	130	0.51
16	1,4-diethenylbenzene	53.87	130	0.50
17	1,1'-(1,2-ethandiyl)bis(4-methyl)benzene	90.74	210	0.37
18	1,3-bis(4-methylphenyl)propane	96.97	224	2.31
19	1,3-bis(2-methylphenyl)propane	97.62	224	2.63
20	1,3-bis(3-methylphenyl)propane	98.30	224	1.18
21	4-methyl-1-{1-[2-(4-methylphenyl)ethyl]vinyl}benzene	100.55	236	10.64
22	1-methyl-1,3-bis(4-methylphenyl)-1-propene	101.42	236	4.22
23	1-methyl-1,3-bis(2-methylphenyl)-2-propene	102.08	236	4.27
24	1-methyl-1-(4-methylphenyl)-3-(2-methylphenyl)propane	103.06	236	3.48
25	tricyclo[10.2.2.25,8]octadeca-5,7,12,14,15,17-hexaene	106.69	236	1.45

TABLE 6.2.11 (continued). *Compounds identified in the pyrogram of poly(vinyl toluene) (mixed isomers) $M_w = 80,000$ shown in Figure 6.2.17.*

Peak	Compound	Ret. Time	MW	Area %
26	2,5-diphenyl-hex-1-ene	107.52	236	0.94
27	analog of tricyclo[10.2.2.25.8]octadeca-5,7,12,14,15,17-hexaene	108.81	236	1.10
28	analog of tricyclo[10.2.2.25.8]octadeca-5,7,12,14,15,17-hexaene	109.78	236	0.72
29	4-[1-methyl-3-(4-methylphenyl)buta-1,3-dienyl]-1-methylbenzene	110.75	248	2.84
30	analog of 4-[1-methyl-3-(4-methylphenyl)buta-1,3-dienyl]-1-methylbenzene	113.02	248	2.20
31	analog of 4-[1-methyl-3-(4-methylphenyl)buta-1,3-dienyl]-1-methylbenzene	113.65	248	2.10
32	analog of 4-[1-methyl-3-(4-methylphenyl)buta-1,3-dienyl]-1-methylbenzene	116.28	248	2.04

The similarity between the pyrolysis products of polystyrene and poly(vinyl toluene) is obvious. The styrene dimer, however, is formed at higher proportion in polystyrene pyrolysis than the dimer of 4-methyl-1-ethenylbenzene in the pyrolysis of poly(vinyl toluene). In addition to the fragments similar to those from styrene but substituted in position 4 of the benzene ring with $-CH_3$, fragments with substitution in position 3 or 2 of the benzene ring also were detected in the pyrogram. Since the polymer contains a mixture of isomers, this isomer mixture in the pyrolysate is expected. A certain degree of crosslinking, for example with divinylbenzene, also may be present in the sample analyzed as pure poly(vinyl toluene).

- Copolymers of alkylstyrenes

Similar to the case of styrene, the copolymers of alkylstyrenes and arylstyrenes are common. The copolymerization is done for the same purposes as for polystyrene, namely to improve/modify certain properties. Copolymerization with divinylbenzene is probably the most frequently utilized. This copolymerization improves mechanical resistance, decreases solubility, and improves thermal resistance. For example, thermal decomposition of poly(vinyltoluene-co-divinyl benzene) 10–50% DVB starts at a higher temperature than that of poly(vinyl toluene). The decomposition at 560°C generates C_1 – C_4 hydrocarbons, benzene, toluene, ethylbenzene, styrene, ethyltoluene, α -methylstyrene, vinyltoluene, divinylbenzene, naphthalene, and ethylstyrene, with a distribution that varies with copolymer composition [71, 118].

In addition to copolymers, various blends containing polyalkylstyrenes are used in practice. One such polymer is poly(4-methoxystyrene) 1/1 w/w blend bisphenol A polycarbonate. The thermal decomposition of this polymer when heated from ambient to 500°C generates CO_2 , 4-methoxystyrene, α -methyl-4-methoxystyrene, p-cresol and small amounts of other phenols, poly(4-methoxystyrene), dimer and trimer with vinylidene and saturated ends, polycarbonate cyclic dimer and chain fragments, bisphenol A, etc. [94].

The results for a Py-GC/MS analysis of a sample of poly(4-ethylstyrene-co-divinylbenzene) with about 80% divinylbenzene, CAS # 9043-77-0, are shown in Figure 6.2.18. The pyrolysis was done on 0.4 mg material at 600°C in He at a heating rate of

20° C/ms with 10 s THT. The separation was done on a Carbowax column similar to other examples previously discussed. The peak identification for the chromatogram shown in Figure 6.2.18 was done using MS spectral library searches only and is given in Table 6.2.12.

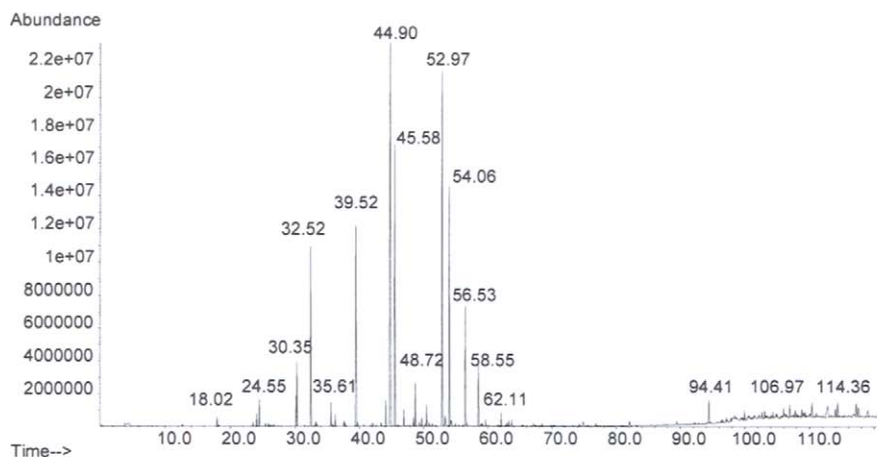


FIGURE 6.2.18. Result for a Py-GC/MS analysis of poly(4-ethylstyrene-co-divinylbenzene) (about 80% divinylbenzene). Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 6.2.12. Compounds identified in the pyrogram of poly(4-ethylstyrene-co-divinylbenzene) (about 80% divinylbenzene) shown in Figure 6.2.18.

Peak	Compound	Ret. Time	MW	Area %
1	1-propene	4.62	42	trace
2	1,2,4-trimethylcyclopentane	8.69	112	trace
3	benzene	12.70	78	trace
4	toluene	18.02	92	0.34
5	ethylbenzene	23.57	106	trace
6	1,4-dimethylbenzene	24.11	106	0.42
7	1,2-dimethylbenzene	24.55	106	0.90
8	1-ethyl-2-methylbenzene	30.19	120	1.01
9	1-ethyl-4-methylbenzene	30.35	120	2.15
10	styrene	32.52	104	6.58
11	1,4-diethylbenzene	35.61	134	0.73
12	1,2-diethylbenzene	36.26	134	0.38
13	(1-methylethenyl)benzene	37.60	118	trace
14	1-ethyl-3-(1-methylethyl)benzene	37.80	148	trace
15	1-ethenyl-3-methylbenzene	39.52	118	9.76
16	1-isopropenyl-4-methylbenzene	44.14	132	0.95
17	4-ethyl-1-ethenylbenzene (monomer)	44.90	132	22.65
18	2-ethyl-1-ethenylbenzene	45.58	132	12.20
19	1-methyl-2-(1-methyl-2-propenyl)benzene	46.94	146	0.51
20	2,3-dihydro-1,3-dimethyl-1H-indene	48.40	146	0.29
21	2,3-dihydro-2,2-dimethyl-1H-indene	48.72	146	1.36

TABLE 6.2.12 (continued). Compounds identified in the pyrogram of poly(4-ethylstyrene-co-divinylbenzene) (about 80% divinylbenzene) shown in Figure 6.2.18.

Peak	Compound	Ret. Time	MW	Area %
22	1,4-dimethyl-2-ethenylbenzene	49.33	132	trace
23	1-ethyl-2,3-dihydroindene	49.73	146	0.26
24	2-methyl-1-butenylbenzene	50.46	146	0.68
25	1,2-dihydronaphthalene	52.97	130	16.76
26	1-ethenyl-2,3-dihydro-1H-indene	53.39	144	0.42
27	1,4-diethenylbenzene	54.06	130	9.02
28	7-methyl-1,2-dihydronaphthalene	54.28	144	trace
29	4-(1-methylvinyl)-1-vinylbenzene	56.53	144	3.95
30	1,3-dimethyl-1H-indene	58.55	144	1.99
31	1,3-bis(1-methylethenyl)benzene	59.62	158	trace
32	6-methyl-1,2-dihydronaphthalene	62.11	144	0.44
33	1,4-bis(1-methylethenyl)benzene	62.95	156	trace
34	1-cyclopentenylbenzene	63.28	144	0.23
35	naphthalene	63.70	128	trace
36	(1-ethylbuta-1,3-dienyl)benzene	67.13	158	trace
37	4-phenyl-3-buten-2-one	74.88	146	trace
38	2,5-cyclohexadien-1-yl-benzene	76.63	156	trace
39	1-(2-propenyl)naphthalene	82.11	168	trace
40	1,2,3,4-tetrahydro-2-phenyl-naphthalene	94.41	208	0.85
41	4-ethyl-1-(3-phenylbutyl)benzene	99.95	238	0.37
42	tricyclo[10.2.2.2<5,8>]octadeca-1(15),5,7,12(16),13,17-hexaene ?	106.97	236	0.62
43	2-methyltricyclo[10.2.2.2<5,8>]octadeca-1(15),5,7,12(16),13,17-hexaene ?	108.81	250	0.38
44	4-ethyl-1-[1-(2-phenylpropyl)vinyl]benzene	110.41	250	0.86
45	C ₂₀ H ₂₂	114.36	262	0.81
46	C ₂₀ H ₂₂	117.22	262	0.85
47	C ₂₁ H ₂₂	117.59	274	0.71
48	C ₂₁ H ₂₄	118.99	276	0.57

Two features are characteristic for the pyrolysis of this copolymer, crosslinking and the existence of mixed isomers regarding the position of the ethyl group. Mixed isomers are obvious from the formation of considerable levels of both 4-ethyl-1-ethenylbenzene and 2-ethyl-1-ethenylbenzene. These compounds indicate that the copolymer was made using 4-ethyl- and also 2-ethyl-styrene. The second feature is the noticeable level of 1,4-diethenylbenzene (about 9%). Some of the bifunctional units will generate 4-ethyl-1-ethenylbenzene and 1,4-diethylbenzene. The formation of the bifunctional monomer has a lower yield compared to that of styrene for the same content in the copolymer.

In addition to the fragments with substitution in position 4 or 2 of the benzene ring, possible substituents in the 3-position were detected in the pyrogram. Since some position isomers are not well distinguished by mass spectral library searches, the precise assignment of this position was not possible. It is likely that the pyrolysis that occurs by a radicalic process leads to the formation of fragment molecules with some modification of the initial structure. The polymer synthesis is also a radicalic process, and some branching of the polymer backbone is not unexpected. From polymers with extensive branching are formed more isomers with the same basic structure.

- Poly(α -methylstyrene)

Poly(α -methylstyrene) $[-C(C_6H_5)(CH_3)-CH_2-]_n$, CAS# 25014-31-7, is a common polymer used in paints (when typically it has low DP), waxes, and adhesives. A number of reports describe the resulting molecules from the pyrolysis of poly(α -methylstyrene) [2, 3, 120, 121], and some describe its thermal decomposition under different heating conditions. Some of these reports are summarized in Table 6.2.13 [48].

TABLE 6.2.13. Summary regarding literature on thermal decomposition of poly(α -methylstyrene).

Polymer	Temp. °C	Results	Ref.
poly(α -methylstyrene)	200–500	95–100% monomer	58
poly(α -methylstyrene)	400–900	benzene, toluene, ethylbenzene, cumene, styrene, α -methylstyrene, indene/phenylpropyne, methyl-1,2-dihydronaphthalene, methyleneindene, naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, biphenyl, anthracene/phenanthrene, dihydropyrene	122
poly(α -methylstyrene)	500 flash in He	toluene, ethylbenzene, 2-propylbenzene, styrene, (1-methylvinyl)benzene, indene, methylindene, 2-propenylbenzene, dimethylnaphthalene, (2-phenylethyl)benzene, (2-phenylvinyl)-benzene, (methyl-2-phenylvinyl)-benzene	2
poly(α -methylstyrene)	520–1200	fragments both larger and smaller than monomer appear in increasing amounts the higher the temperature, particularly CH_4 , C_2H_4 , and C_6H_6 until at 1200° C the monomer yield is only 33.9%	58

A pyrogram for poly(α -methylstyrene) is shown in Figure 6.2.19. The pyrolysis was done at 600° C in He at a heating rate of 20° C/msec. The separation was done on a Carbowax column (60 m, 0.32 mm i.d., 0.32 μ m film thickness) with the GC starting at 40° C with a ramp of 2° C/min. up to 240° C and a final oven time of 20 min. The MS was operated in EI+ mode.

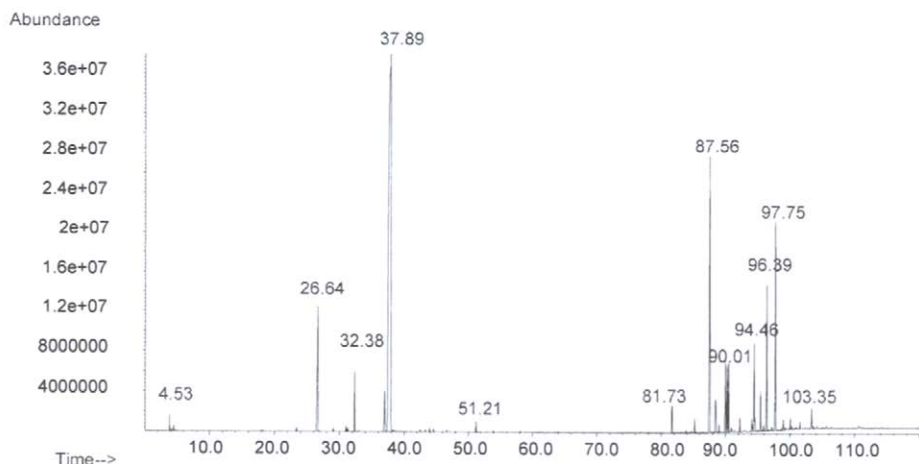


FIGURE 6.2.19. Result for a Py-GC/MS analysis of poly(α -methylstyrene) $M_n = 790$. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 6.2.14. Compounds identified in the pyrogram of poly(α -methylstyrene) as shown in Figure 6.2.19.

Peak	Compound	Ret. Time	MW	Area %
1	2-methyl-1-propene	4.53	56	0.32
2	benzene	12.56	78	trace
3	toluene	17.85	92	trace
4	water	18.21	18	trace
5	ethylbenzene	23.41	106	trace
6	(1-methylethyl)benzene	26.64	120	4.87
7	propylbenzene	29.07	120	trace
8	(1,1-dimethylethyl)benzene	31.05	134	0.18
9	(2-methylpropyl)benzene	31.24	134	trace
10	styrene	32.38	104	1.80
11	(2-methyl-2-propenyl)benzene	37.01	132	2.03
12	α -methylstyrene	37.89	118	48.82
13	(2-propenyl)benzene	42.51	118	trace
14	(2-methyl-1-propenyl)benzene	43.34	132	trace
15	methyl(1-methylethenyl)benzene	43.98	132	trace
16	1-methyl-4-(1-methylethenyl)benzene ?	44.61	132	trace
17	(1,3-dimethyl-3-butenyl)benzene	46.71	160	trace
18	(1-methylbutyl)benzene ?	51.21	148	0.33
19	(1,1-dimethyl-2-butenyl)benzene	53.88	158	trace
20	benzenemethanol ?	64.00	136	trace
21	1,1'-(1-methyl-1,2-ethanediyl)bis-benzene	81.73	196	0.88
22	2-methyl-9,10-dihydroanthracene	83.88	194	trace
23	1,1'-(1,1,2,2-tetramethyl-1,2-ethandiyl)bis-benzene	84.72	238	trace
24	2,3-dihydro-1,1,3-trimethyl-3-phenyl-1H-indene	87.57	236	12.05
25	unknown hydrocarbon	88.48	222	1.98
26	unknown hydrocarbon	89.03	194	0.27
27	(1-methyl-3-phenyl-2-butenyl)benzene	90.01	222	2.25
28	isomer of (methylphenyl-?-butenyl)benzene	90.30	222	2.12
29	1,1'-(3,3-dimethyl-1-butenyldiene)bis-benzene	90.52	236	2.20
30	unknown hydrocarbon	92.25	238	0.53
31	unknown hydrocarbon	94.11		0.54
32	2,4-diphenyl-4-methyl-1-pentene (dimer)	94.46	236	3.36
33	1,1-diphenyl-1,3-pentadiene	95.45	220	1.39
34	2,4-diphenyl-4-methyl-2-pentene	96.40	236	4.99
35	2,4-diphenyl-4-ethyl-1-pentene + unknown	97.75	250	7.74
36	unknown hydrocarbon	99.00	250	0.50
37	unknown hydrocarbon	103.35	250	0.83

The peak identification for the chromatogram shown in Figure 6.2.19 was done using MS spectral library searches and is shown in Table 6.2.14. Sometimes MS spectral library searches give results bearing some ambiguity. For example, the spectrum of the peak eluting at 87.56 min. can be either that of 2,3-dihydro-1,1,3-trimethyl-3-phenyl-1H-indene, or 1,1'-(1,3,3-trimethyl-1-propene-1,3-diyl)bisbenzene. The three spectra, one for the unknown and the other for two possible matches, are shown in Figure 6.2.20.

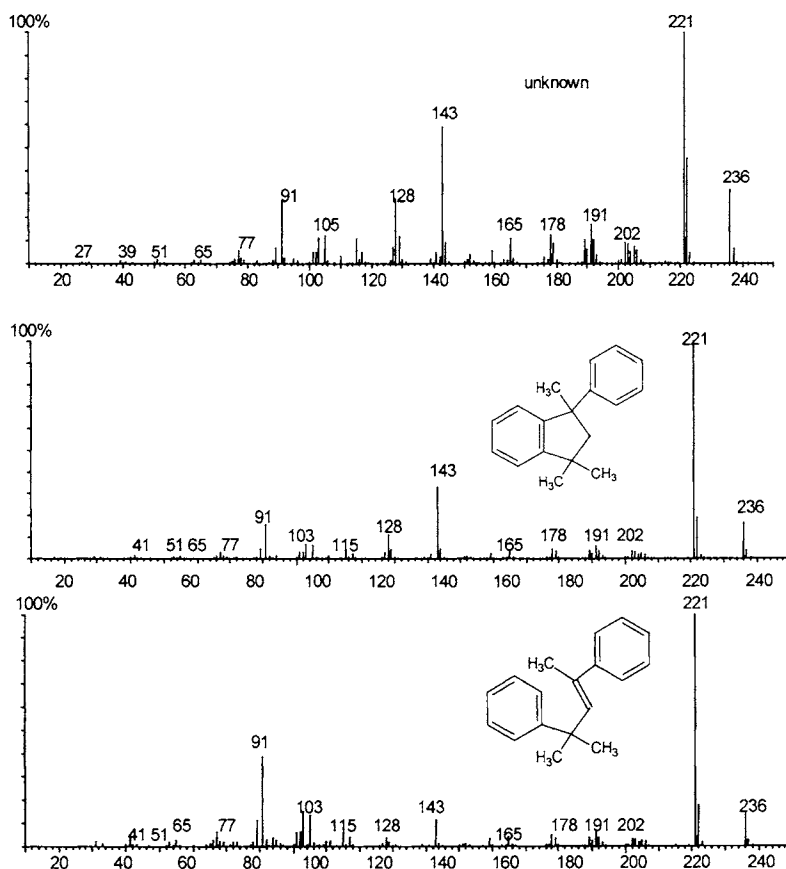


FIGURE 6.2.20. Mass spectrum of peak eluting at 87.57 min. in the pyrogram shown in Figure 6.2.19 and the mass spectra of 2,3-dihydro-1,1,3-trimethyl-3-phenyl-1H-indene (80% match) and of 1,1'-(1,3,3-trimethyl-1-propene-1,3-diyl)bisbenzene (70% match).

As seen in Table 6.2.14, the yield of monomer for poly(α -methylstyrene) is higher than that of polystyrene. Pyrolysis process takes place with random initiation and with intense β -scission (relative to the radical bearing atom). Other compounds identified in the pyrolysate are mainly molecules with one or two benzene rings. They are generated from different fragmentations of the polymeric backbone. Only traces of benzene are seen in the pyrogram, indicating very limited fragmentation of the side groups. Water comes probably from the surface of the polymer.

Similarly to polystyrene, poly(α -methylstyrene) can be obtained as head to tail polymer (H-T) and also as head to head (H-H), the common material being the H-T form. The pyrolysis products of the two forms show some differences in the dimer area, the H-H form indicating the presence of 2,5-diphenylhexane and 2,5-diphenyl-1-hexene [3].

Thermal properties of some copolymers of poly(α -methylstyrene) are reported in literature, an example being poly(α -methylstyrene-co-methyl methacrylate) [100]. Thermal decomposition of poly(vinyl chloride)-blend-poly(α -methylstyrene) when heated between ambient to 500°C also is reported [106]. In these conditions, the polymer generates mainly HCl and α -methylstyrene. Other pyrolysis studies are also available [100, 123–125].

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6.3 HALOGENATED POLYOLEFINS

- General aspects

Halogenated polyolefins form another class of polymers. Some of the polymers from this class have important practical applications. Among these are poly(vinyl chloride), poly(vinylidene chloride), and polytetrafluoroethylene. Several unusual polymers such as poly(vinyl bromide) also are included in this class. Most halogenated polymers are obtained by the polymerization of a halogenated monomer. However, chemical modification (e.g. chlorination) of a preexistent polymer also can be applied to obtain partially halogenated materials.

Some of the halogenated polyolefins are vinyl derivatives such as poly(vinyl chloride) and poly(vinyl fluoride), some are vinylidene derivatives, and others are polymers with even higher levels of halogenation. For example, from monomers of fluorinated ethylenes, the following polymers can be obtained:



In addition to homopolymers containing only fluorine or chlorine atoms, polyolefins with different halogens in the monomeric unit can be synthesized. This group includes polymers such as poly(chlorotrifluoroethylene) or KEL-F, poly(1,1-dichloro-2,2-difluoroethylene), etc. Polymers containing fluorine, chlorine, and hydrogen atoms attached to the carbon backbone also are known. Besides halogenated polyethylenes, polymers such as poly(perfluoro-heptene) or poly(perfluoro-propylene) are used in practice. The copolymers with alternating halogen-substituted ethylene and ethylene monomers, such as poly(ethylene-*alt*-trifluorochloro-ethylene) with the structure $[-\text{CH}_2\text{CH}_2-\text{CF}(\text{Cl})\text{CF}_2-]_n$ also are included in this class.

- Poly(vinyl chloride)

Poly(vinyl chloride) or PVC, CAS# 9002-86-2 (other CAS# also are registered, e.g. 26793-37-3 for isotactic polymer), has the general formula $[-\text{CH}_2\text{CH}(\text{Cl})-]_n$. The polymer has a low cost and a variety of applications due to its valuable qualities such as toughness, abrasion resistance, chemical resistance, as well as self-extinguishing properties. PVC is used for injection molded or extruded components, pipes, insulating materials for electrical wires and equipment, furniture, building materials, etc. It is used in films for packaging purposes, for fibers, and even for foams used for insulation. Poly(vinyl chloride) and some of its copolymers are frequently treated with plasticizers such as dialkylphthalates (ethylhexyl, butyl), dioctyl sebacate, dioctyl adipate, or with low molecular weight poly(propylene glycol). The addition of plasticizers improves many properties of PVC.

The polymer is commonly obtained from vinyl chloride with a peroxide initiator such as peroxydicarbonates, *tert*-butylperpivalate, benzoyl or lauroyl peroxide, acetyl cyclohexylsulfonyl peroxide, or azobis(2,4-dimethylvaleronitrile). The polymerization can be done by suspension, emulsion or solution techniques. Low polymerization temperatures are used when high MW material is required. Suspension polymerization employs water suspension agents, such as poly(vinyl alcohol) or methylcellulose. The resulting polymer is a partially syndiotactic material but with low crystallinity. The macromolecules typically have head to tail linkages (H-T) and a small proportion (less than 1.5%) of branching. Ziegler-Natta catalysts are not used to produce PVC.

PVC is relatively unstable to heat, and at temperatures as low as 200° C begins to decompose. The decomposition of PVC has a complex chemical mechanism [1] and takes place in two steps, the first being dehydrochlorination, and the second being the

tar release and residue char formation. Dehydrochlorination starts above 200° C before breaking the carbon backbone. Above 300° C the formation of unsaturated conjugated hydrocarbons is noticeable. Above 400° C benzene and other aromatic hydrocarbons are detected [2, 3]. The decomposition probably takes place with a free radical mechanism. The HCl formed in the reaction may autocatalyze further decomposition, and ionic complexes also may be involved in the process [4]. The decomposition in oxygen starts with darkening, the oxygen being involved in scissions and crosslinking reactions. Because the HCl accelerates the thermal decomposition, in practice the polymer has added stabilizers that scavenge the HCl that can be formed by heating. Even common processing, which is done with heat, requires stabilizers to avoid discoloration and progressive deterioration [5]. Numerous other studies are related to PVC thermal decomposition in various conditions including addition of stabilizers, presence of other small molecules such oxides and salts, and presence of materials acting only by surface contacts [6–18]. Results from several studies on thermal decomposition of the polymer are summarized in Table 6.3.1 [19].

TABLE 6.3.1. Summary regarding literature information on thermal decomposition of poly(vinyl chloride), CAS# 9002-86-2.

Polymer	Temp. °C	Results	Ref.
poly(vinyl chloride)	200–300	quantitative yields of HCl	2
poly(vinyl chloride)	400	saturated and unsaturated, aliphatic and aromatic hydrocarbons are produced, with benzene and toluene in high yield	2
poly(vinyl chloride)	500	propane, butene, benzene, toluene, ethylbenzene, xylenes, indane, indene, propylbenzene, butenylbenzene, methylindane, divinylbenzene, naphthalene, methylnaphthalene, dimethylnaphthalene, biphenyl, methylbiphenyl, 2-phenylethylbenzene	20
poly(vinyl chloride)	600	In helium; quantitative yield of HCl, remainder residue and hydrocarbons; benzene is major volatile hydrocarbons product	21
poly(vinyl chloride)	280–800	aliphatic hydrocarbons, benzene (major product), toluene, ethylbenzene, o-xylene, monochlorobenzene, styrene, vinyl toluene, p-dichlorobenzene, o-dichlorobenzene, indene, 1,3,5-trichlorobenzene, 1,2,4-trichlorobenzene, naphthalene, α -methylnaphthalene, β -methylnaphthalene; effect of ZnO, SnO ₂ , and Al ₂ O ₃ on the yields of products is also recorded	3.
poly(vinyl chloride)	ambient to 1000	HCl, CO ₂ , ethene, ethane, propane, 1-butene, 2-butene, 1-pentene, cyclopentene, n-pentane, 2-methylbutane, 1,3-pentadiene, 2-methyl-1,3-pentadiene, complex series (60 identified) of aromatic and polyaromatic species including benzene, styrene, methylstyrenes, toluene, o-xylene, m-xylene, p-xylene, biphenyl, naphthalene, anthracene, phenanthrene, pyrene, etc.	22

Depending on the polymer sample (and presence of various stabilizers), as well as the heating conditions, thermal decomposition of PVC may show some variations. The curve showing the variation of weight loss % as a function of temperature (TG curve) for a 3.5 mg PVC sample with $M_w = 85,000$ is shown in Figure 6.3.1. The heating was done between 30° C and 830° C at a rate of 10° C/min. in air.

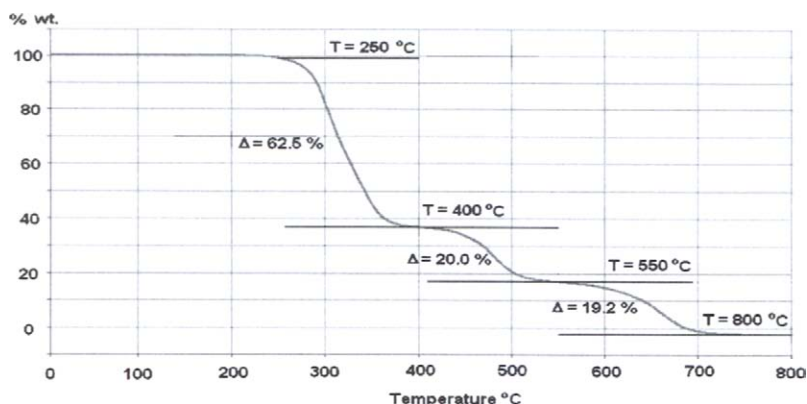


FIGURE 6.3.1. Variation of weight % loss for a poly(vinyl chloride) sample in a TGA experiment at a heating rate of 10°C/min .

The thermogram shows three different processes. The first process is caused mainly by the elimination of HCl (the formation of a molecule of HCl represents 58.4% weight loss). The second process leads to formation of char and of unsaturated and aromatic hydrocarbons that are volatile and can be detected by gas chromatography. One more step can be seen in the TGA trace, when the weight of the sample is reduced to zero due to the oxidation of char with the oxygen present in the atmosphere of the heating device and due to some residual compounds volatile at elevated temperatures (a slight decrease below 0% weight is due to an experimental imprecision).

The main characteristics of the pyrolysis of PVC are the formation of HCl and that of unsaturated and aromatic hydrocarbons (a few partially chlorinated). This is the result of the formation of double bonds by the elimination of HCl followed by the breaking of the carbon chain with or without cyclization. The results for a Py-GC/MS analysis of a poly(vinyl chloride) sample are shown in Figure 6.3.2. The pyrolysis was done at 600°C in He at a heating rate of 20°C/msec with 10 sec. THT. The separation was done on a Carbowax column (60 m, 0.32 mm i.d., 0.32 μm film thickness) with the GC starting at 40°C with a ramp of 2°C/min . up to 240°C and a final oven time of 20 min. (see Table 4.2.2). The MS was operated in EI+ mode. The peak identification for the chromatogram shown in Figure 6.3.2 was done using MS spectral library searches and is given in Table 6.3.2. Most peak identifications were obtained with high probability for the search results.

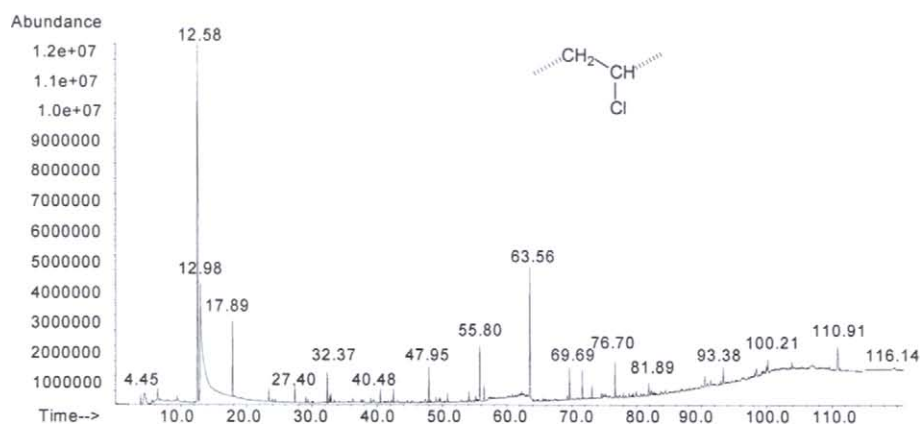


FIGURE 6.3.2. Result for a Py-GC/MS analysis of poly(vinyl chloride) $M_w = 85,000$. Pyrolysis done on 0.4 mg material at 600°C in He, with the separation on a Carbowax type column.

TABLE 6.3.2. Compounds identified in the pyrogram of poly(vinyl chloride) shown in Figure 6.3.2.

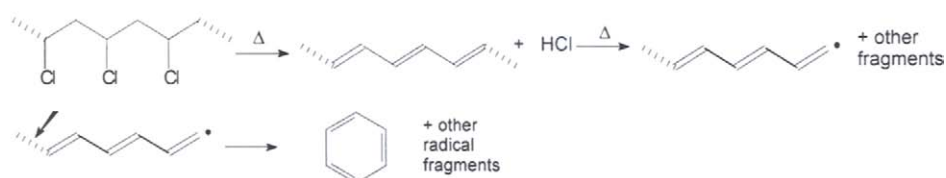
Peak	Compound	Ret. Time	MW	Area %
1	ethane	4.37	30	trace
2	1-propene	4.45	42	1.17
3	2-methyl-1-propene	4.56	56	trace
4	1,3-butadiene	4.70	54	trace
5	vinyl chloride	4.94	62	trace
6	cyclopentene	5.58	68	trace
7	1,3-cyclopentadiene	6.46	66	1.09
8	1,3,5-hexatriene	9.41	80	trace
9	benzene	12.58	78	22.27
10	hydrochloric acid	12.98	36	34.17
11	toluene	17.89	92	4.63
12	ethylbenzene	23.44	106	0.74
13	1,2-dimethylbenzene	23.95	106	trace
14	1,3-dimethylbenzene	24.40	106	trace
15	1,4-dimethylbenzene	27.40	106	1.08
16	propylbenzene	29.04	120	trace
17	chlorobenzene	29.42	112	trace
18	styrene	32.37	104	1.62
19	1-ethyl-2-methylbenzene	32.74	120	0.38
20	2-propenylbenzene	32.94	118	0.48
21	butylbenzene	36.25	134	trace
22	1-propenylbenzene	37.53	118	trace
23	indane	40.48	118	0.74
24	1-ethenyl-2-methylbenzene	42.48	118	0.77
25	1H-indene	47.95	116	2.00
26	4-methyl-2,3-dihydro-1H-indene	49.02	132	trace
27	1,2,3,4-tetrahydronaphthalene	50.80	132	0.47
28	2-methylindene	54.13	130	0.63

TABLE 6.3.2 (continued). Compounds identified in the pyrogram of poly(vinyl chloride) shown in Figure 6.3.2.

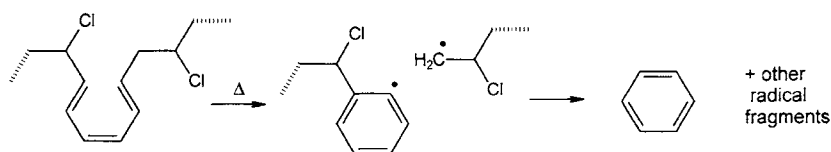
Peak	Compound	Ret. Time	MW	Area %
29	1-methyl-1H-indene	55.16	130	0.37
30	1,2-dihydronaphthalene	55.80	130	3.26
31	1,4-dihydronaphthalene	56.48	130	0.88
32	naphthalene	63.56	128	8.20
33	1-methylnaphthalene	69.69	142	2.02
34	2-methylnaphthalene	71.65	142	1.71
35	2-methyl-1,1'-biphenyl	73.13	168	0.76
36	1-ethylnaphthalene	74.56	156	trace
37	biphenyl	76.70	154	1.92
38	1,1'-methylenebis-benzene	77.98	168	trace
39	acenaphthene	79.97	154	0.27
40	2-ethylnaphthalene	81.90	154	0.98
41	4-methyl-1,1'-biphenyl	81.96	168	0.27
42	3-methyl-1,1'-biphenyl	90.54	168	0.85
43	1-methyl-9H-fluorene	91.45	180	0.41
44	fluorene	93.38	166	1.00
45	2-methyl-9H-fluorene	98.46	180	0.86
46	1,2,3,4-tetrahydrophenanthrene	99.97	182	0.36
47	(E)-stilbene	100.21	180	0.98
48	9,10-dihydrophenanthrene	103.89	180	0.52
49	phenanthrene	110.91	178	2.11
50	1-methylanthracene	116.14	192	0.02

Benzene is a major component in PVC pyrolysis. Other aromatic components also are present. In addition to the compounds indicated in Table 6.3.2, heavier aromatic compounds such as naphthacene and benzo[b]phenanthrene were indicated in PVC pyrolysates [23]. Also, a more complete list of aromatic compounds generated in pyrolysis during non-flaming burning of PVC is reported in literature [24]. Compounds with two, three, four aromatic cycles and even benzo[ghi]perylene (six cycles) are included in this list.

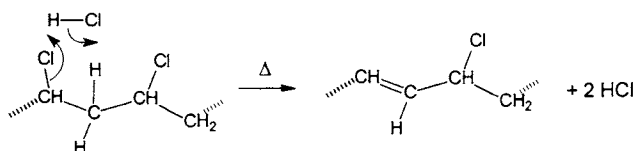
The formation of aromatic compounds in PVC pyrolysis is schematically exemplified for benzene:



The polyene also can generate benzene from segments with partially eliminated HCl by the following mechanism:

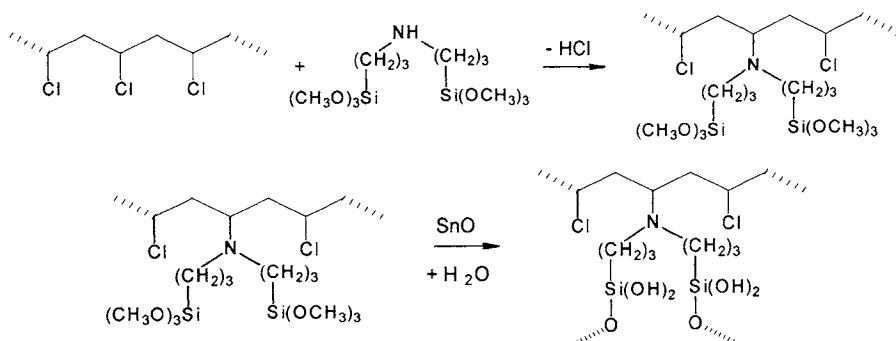


Both free radical and molecular elimination mechanisms seem to participate in PVC degradation. After the initial formation of some HCl molecules, these seem to have a catalytic effect on the decomposition of PVC, which can be explained by reactions of the type [25]:



Char formation in PVC pyrolysis can be explained by further dehydrogenation of the polyunsaturated molecules generated by HCl elimination.

Thermal stability of PVC can be modified using crosslinking agents. For example, crosslinking can be done with amino silanes such as bis(γ -trimethoxysilylpropyl)amine followed by reaction with traces of water in the presence of an oxide used as catalyst [26]. The reactions taking place in this case are shown below:



The thermal properties of the resulting polymer can be modified by using different proportions of crosslinking agents.

- Copolymers of vinyl chloride

Vinyl chloride is used as a comonomer in many copolymers. For example, copolymers with acrylonitrile are used in the manufacturing of fibers, and those with acrylates and

methacrylates are used in paints, adhesives and various types of rubbery materials. Some copolymers are designed to increase PVC thermal stability. Special low flammability fibers are made from copolymers of vinyl chloride and vinyl alcohol. Blends including poly(vinyl chloride) are also common. Poly(vinyl chloride)/acrylic-styrene-acrylonitrile terpolymer blends are used in automotive and marine industries for coatings. Other blends include those with bisphenol A polycarbonate, with nitrile rubber (acrylonitrile butadiene copolymer), with poly(methyl methacrylate), with poly(methyl methacrylate-co-methyl acrylate), with poly(methyl methacrylate-co-ethyl acrylate), with poly(methyl methacrylate-co-butyl acrylate), with poly(methyl methacrylate-co-ethylhexyl acrylate), etc.

Thermal stability of vinyl chloride copolymers is usually better than that of the homopolymer [27]. Some pyrolysis studies on PVC copolymers are reported in literature [28–32]. A summary of several thermal stability studies of poly(vinyl chloride) copolymers are indicated in Table 6.3.3.

TABLE 6.3.3. Summary regarding literature information on thermal decomposition of copolymers of vinyl chloride [19].

Polymer	Temp. °C	Results	Ref.
poly(methyl methacrylate)-blend-poly(vinyl chloride)	ambient to 500	major products: HCl, methyl methacrylate; minor products: CO ₂ , methyl chloride, benzene	33, 34
poly(vinyl acetate)-blend-poly(vinyl chloride)	ambient to 500	acetic acid, HCl, and traces of CO ₂ , ketene, acetyl chloride, CO and CH ₄	35
poly(vinyl acetate-co-vinyl chloride)	ambient to 500	bulk polymer; HCl and acetic acid in the proportions of the monomers in the copolymer; at each end of the composition range, incorporation of the comonomer results in a copolymer less stable than the homopolymer; minimum stability at 40-50 mol% vinyl acetate	36
poly(vinyl acetate-co-vinyl chloride)	200-450	similar decomposition with homopolymers generating HCl and acetic acid followed by the formation of aromatic hydrocarbons from the backbone scission; an induction period similar to homopolymers is also noticed because after the elimination of a small molecule from the side chain the chain is destabilized	14

The results for a Py-GC/MS analysis of a poly(vinyl chloride-co-vinyl acetate) 86 wt % vinyl chloride sample are shown in Figure 6.3.3. The polymer has the CAS# 9003-22-9, the idealized formula $[-CH_2CH(Cl)-]_x [-CH_2CH(OCOCH_3)-]_y$ and $M_n = 27,000$. The pyrolysis was done at 600° C in He at a heating rate of 20° C/msec with 10 sec. THT. The separation was done on a Carbowax column (60 m, 0.32 mm i.d., 0.32 µm film thickness) with the GC starting at 40° C with a ramp of 2° C/min. up to 240° C and a final oven time of 20 min. The MS was operated in EI+ mode. The peak identification for the chromatogram shown in Figure 6.3.3 was done using MS spectral library searches only and is given in Table 6.3.4.

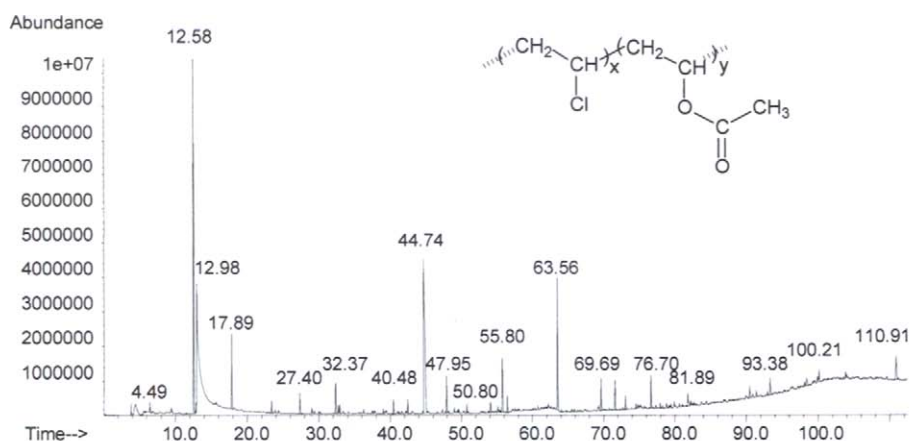


FIGURE 6.3.3. Result for a Py-GC/MS analysis of poly(vinyl chloride-co-vinyl acetate) with 86 wt % vinyl chloride, $M_n = 27,000$. Pyrolysis done on 0.4 mg material at 600°C in He, with the separation on a Carbowax type column.

TABLE 6.3.4. Compounds identified in the pyrogram of poly(vinyl chloride-co-vinyl acetate) with 86 wt % vinyl chloride, shown in Figure 6.3.3.

Peak	Compound	Ret. time	MW	Area %
1	carbon dioxide	4.28	44	0.46
2	1-propene	4.49	42	0.75
3	2-methyl-1-propene	4.56	56	trace
4	1,3-butadiene	4.70	54	trace
5	1,3-pentadiene	5.62	68	trace
6	1,3-cyclopentadiene	6.46	66	0.52
7	1,3,5-hexatriene	9.45	80	trace
8	benzene	12.58	78	20.88
9	2-methyl-1,3-dioxolane ?	12.90	88	0.38
10	hydrochloric acid	12.98	36	27.93
11	toluene	17.89	92	3.96
12	ethylbenzene	23.44	106	0.62
13	1,2-dimethylbenzene	23.95	106	trace
14	1,3-dimethylbenzene	24.40	106	trace
15	1,4-dimethylbenzene	27.40	106	0.96
16	propylbenzene	29.04	120	trace
17	chlorobenzene	29.42	112	trace
18	styrene	32.37	104	1.34
19	2-propenylbenzene	32.93	118	0.40
20	indane	40.48	118	0.64
21	1-ethenyl-2-methylbenzene	42.47	118	0.64
22	acetic acid	44.74	60	15.73
23	1H-indene	47.95	116	1.76
24	1,2,3,4-tetrahydronaphthalene	50.80	132	0.41
25	2-methylindene	54.12	130	0.53
26	1,2-dihydronaphthalene	55.80	130	2.73
27	1,4-dihydronaphthalene	56.48	130	0.78
28	naphthalene	63.56	128	6.90
29	1-methylnaphthalene	69.69	142	1.75

TABLE 6.3.4 (continued). Compounds identified in the pyrogram of poly(vinyl chloride-co-vinyl acetate) with 86 wt % vinyl chloride, shown in Figure 6.3.3.

Peak	Compound	Ret. time	MW	Area %
30	2-methylnaphthalene	71.65	142	1.43
31	2-methyl-1,1'-biphenyl	73.12	168	0.70
32	biphenyl	76.70	154	1.57
33	2-ethylnaphthalene	81.88	154	0.85
34	3-methyl-1,1'-biphenyl	90.52	168	0.70
35	fluorene	93.38	166	0.95
36	2-methyl-9H-fluorene	98.44	180	0.75
37	(E)-stilbene	100.21	180	0.81
38	9,10-dihydrophenanthrene	103.88	180	0.37
39	phenanthrene	110.91	178	1.81

Except for the acetic acid peak, the pyrogram of poly(vinyl chloride-co-vinyl acetate) is very similar to that of poly(vinyl chloride). However, this is easily explained by the fact that both poly(vinyl chloride) and poly(vinyl acetate) homopolymers have a similar pyrolysis mechanism, with the elimination of side chain groups and formation of double bonds along the polymeric backbone. After the acetic acid and/or HCl elimination the remaining polymeric structure undergoes the same process of formation of unsaturated and aromatic molecules. This explains the presence of a number of aromatic compounds that are identical in the pyrolysate of the two homopolymers (see Section 6.5 for the pyrolysis of poly(vinyl acetate)).

The results for a Py-GC/MS analysis of a poly(vinyl chloride-co-acrylonitrile) 20 wt % acrylonitrile sample are shown in Figure 6.3.4. The polymer has the CAS# 9010-76-8, the idealized formula $[-CH_2CH(Cl)-]_x [-CH_2CH(CN)-]_y$ and $M_w = 150,000$. The pyrolysis and the separation conditions were the same as for poly(vinyl chloride) (see Table 4.2.2). The peak identification for the chromatogram shown in Figure 6.3.4 was done using MS spectral library searches only and is given in Table 6.3.5.

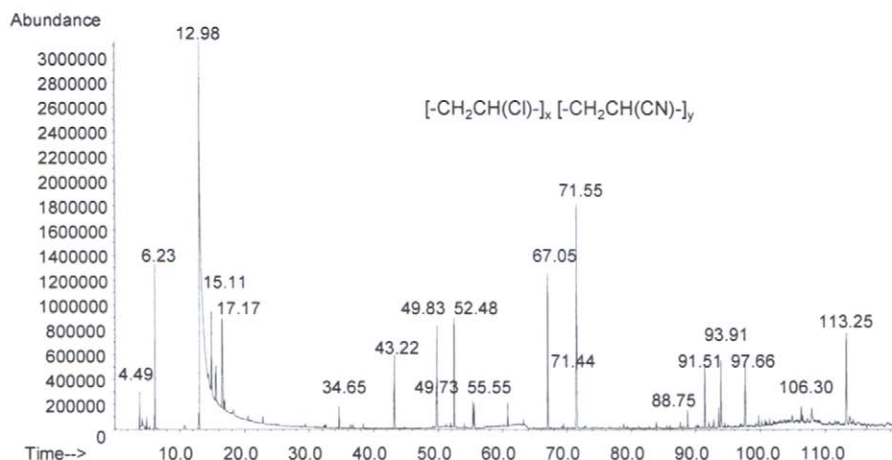


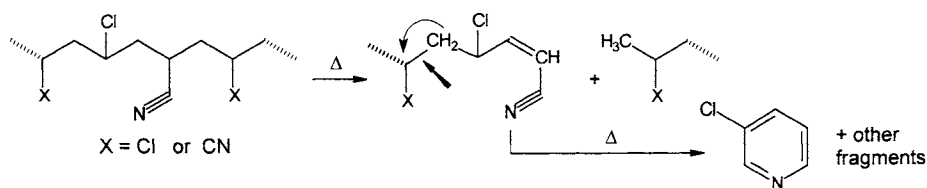
FIGURE 6.3.4. Result for a Py-GC/MS analysis of poly(vinyl chloride-co-acrylonitrile) 20 wt % acrylonitrile, $M_w = 150,000$. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 6.3.5. Compounds identified in the pyrogram of poly(vinyl chloride-co-acrylonitrile) 20 wt % acrylonitrile, $M_w = 150,000$, shown in Figure 6.3.4.

Peak	Compound	Ret. time	MW	Area %
1	1-propene	4.49	44	0.42
2	chloroethane	4.90	62	trace
3	2,3-dimethylbutene	4.97	84	trace
4	2-chloropropene	5.39	84	trace
5	1,1-dichloroethene	6.23	96	2.74
6	2-methyl-1,3-dioxolane ?	12.90	88	0.70
7	hydrochloric acid	12.98	36	49.82
8	2-methyl-2-propenenitrile	14.46	76	0.40
9	acrylonitrile	15.11	53	3.21
10	acetonitrile	15.79	41	1.31
11	hydrocyanic acid	16.73	27	trace
12	propanenitrile	17.17	55	3.35
13	2,3-dichloro-1-propene	20.49	110	trace
14	1,4-dichloro-1,3-butadiene	22.89	122	trace
15	chlorobenzene	29.44	112	trace
16	styrene	32.37	104	trace
17	2-methyl-1,1,3-trichloropropene+ impurity	34.65	158	0.54
18	3-methyl-chlorobenzene	36.36	126	trace
19	2,4-pentadienenitrile	36.84	79	trace
20	1,2,3-trichloropropene ?	38.38	144	trace
21	1,3-dichlorobenzene	43.22	146	2.02
22	1-methyl-3,5-dichlorobenzene	49.73	160	0.89
23	1,3,5-trichlorobenzene	49.83	180	3.00
24	2-chloropyridine	52.48	113	3.10
25	benzonitrile	55.55	103	0.70
26	3-chloropyridine	55.59	113	0.65
27	2-chlorobenzonitrile	58.20	137	trace
28	4-methylbenzonitrile	61.00	117	0.60
29	3-chlorobenzonitrile	67.05	137	4.70
30	2-methyl-5-chlorobenzonitrile	71.44	151	1.37
31	3,5-dichlorobenzonitrile	71.55	171	6.92
32	2-methylenepentanedinitrile	78.84	106	trace
33	pentanedinitrile	84.45	94	trace
34	3-hexenedinitrile	85.98	106	trace
35	3,5-dichlorobenzylamine ?	88.75	175	0.54
36	1,4-benzendicarbonitrile	91.51	128	1.91
37	α -dicyanotoluene	93.55	142	0.57
38	chloronaphthalene	93.91	162	2.12
39	2,3,6-trichloronaphthalene + dichlorodimethylbenzene	97.66	230, 174	2.80
40	2,3,6-trichloronaphthalene	106.30	230	0.58
41	3,6-dichloroquinoline	107.92	197	0.59
42	tetrachloronaphthalene	113.25	264	4.46

Some of the compounds generated during the pyrolysis of poly(vinyl chloride-co-acrylonitrile) are similar to those from the homopolymers. More aromatic compounds with chloro groups are generated from the copolymer than from the poly(vinyl chloride). The copolymer behaves as if the CN groups are more easily eliminated than chlorine groups, although polyacrylonitrile as a homopolymer decomposes at a considerably higher temperature compared to poly(vinyl chloride). Some compounds resulting from the cyclization of the unsaturated chain, including nitrogen in the cycle and with attached

chlorine groups also are present. These compounds are formed in reactions similar to the one shown below for the formation of 3-chloropyridine:



Compounds such as 3-chloropyridine or 3,6-dichloroquinoline are proof of the random structure of the copolymer.

- Poly(vinylidene chloride) and its copolymers

Another chlorinated polyolefin is poly(vinylidene chloride) or poly(1,1-dichloroethylene), PVDC, which has the general formula $[-CH_2C(Cl)_2-]_n$ and CAS# 9002-85-1 and 98846-23-2. This polymer is used in adhesives and as copolymer with PVC and other polymers, conferring low permeability for example for films of polyethylene or polypropylene (barrier films). Poly(vinylidene chloride) is relatively unstable at heating, the elimination of HCl starting as low as 140° C. The decomposition is more advanced between 210° C to 225° C when the polymer changes its color to brown, probably due to the formation of conjugated double bonds in the chain. Unsaturated or aromatic hydrocarbons similar to those formed from poly(vinyl chloride) are formed at higher temperatures. Some literature reports discussing the thermal decomposition of poly(vinylidene chloride) between 225 °C and 275 °C indicate the formation of high yields of HCl [37]. The decomposition of the polymer around 170° C in the presence of oxygen generates phosgene, formaldehyde, and HCl [38]. Other reports also were published [39, 40].

A number of copolymers of vinylidene chloride are used in practice. Copolymers with acrylonitrile are used in low flammability fibers (modacrylic fibers). These fibers begin to lose weight when heated at 285–308° C due to dehydrohalogenation [41] but do not ignite easily. A tercopolymer butadiene-styrene-vinylidene chloride is used in fabrics industry and in paper industry. Other copolymers include PVC/PVDC, used for fibers and for films with low permeability to gases and water vapors (barrier films), etc.

- Poly(vinyl fluoride)

Several poly(fluorinated olefins) are used in practice. These include poly(vinyl fluoride), poly(vinylidene fluoride), poly(trifluoroethylene), poly(tetrafluoroethylene), and other fluorinated polyolefins such as poly(perfluoro-heptene) or poly(perfluoro-propylene). Poly(vinyl fluoride) with the general formula $[-CH_2CHF-]_n$ and CAS# 24981-14-4 is less common than its chlorinated analog, but still has numerous practical applications, mainly in coatings. Upon heating, the polymer begins losing HF at about 350° C with formation of double bonds in the carbon chain. At about 450° C the backbone of the polymer

starts breaking, with the formation of compounds similar to those of poly(vinyl chloride), namely unsaturated olefins and, depending on the temperature, aromatic compounds. The char formed up to 650° C is further decomposed at higher temperatures, leaving only carbon. As a general rule, the elimination of a hydrohalogen acid occurs easily when a hydrogen is present at the α -carbon vs. the carbon where the halogen is substituted. Although the enthalpy of formation (see Section 2.2) decreases in absolute value from HF to HCl, to HBr, and is the lowest for HI, the elimination of HI and HBr occurs very easily, while the elimination of HF is more difficult (HF is a poor leaving group compared to HBr, for example). This makes the fluorinated compounds more stable to heat compared to chlorinated or brominated ones. Among some literature reports discussing thermal decomposition of poly(vinyl fluoride), all indicate the formation of HF with high yields. In addition to HF it is reported that heating of the polymer between 372° C and 480° C generates products nonvolatile at 25° C and little carbonization [42]. Heating in the range 200° C to 500° C generates HF and C₂-C₉ fractions [43]. Heating at 450° C results in 85% wt. loss, 33 \pm 5% volatile products, with the remainder an oily green liquid. Volatile products consist of HF (82 mol%), CH₄ (5.2 mol%), C₂H₆ (0.6 mol%), ethylene (0.8 mol%), acetylene (0.03 mol%), fluoroethylene (0.07 mol%), propene (0.5 mol%), C₃H₅F (0.4 mol%), butane (0.06 mol%), butene (1.1 mol%), 1,3-butadiene (0.7 mol%), C₄H₅F (0.06 mol%), cyclopentadiene (0.05 mol%), benzene (4.5 mol%), fluorobenzene (0.3 mol%), toluene (1.0 mol%), C₆H₄(CH₃)F (0.04 mol%), C₆H₅C₂H₅ or C₆H₄(CH₃)₂ and styrene (0.9 mol%), n-propylbenzene (0.2 mol%), isopropylbenzene (0.3 mol%), C₆H₅-C₃H₅ (0.2 mol%), indene (0.3 mol%), naphthalene (0.8 mol%), fluoronaphthalene (0.3 mol%) [44].

- Poly(vinylidene fluoride) and poly(trifluoroethylene)

Poly(vinylidene fluoride) or poly(1,1-difluoroethylene), with the general formula [-CH₂CF₂-]_n and CAS# 24937-79-9, is a polymer used for metal coatings, particularly when a chemically resistant surface is necessary, in cable insulations, in various copolymers, etc. The thermal degradation of this polymer starts at a higher temperature compared to its chlorinated homolog. The decomposition with the elimination of HF starts around 380–390° C. The process continues with backbone cleavage and frequently with the formation of cyclic aromatic compounds such as trifluorobenzene. Some literature reports discussing the thermal decomposition of poly(vinylidene fluoride) indicate that heating between 400° C and 530° C generates 35% HF and high yields of products that are nonvolatile at 25° C plus some carbonization [42]. Heating from ambient to 500° C generates monomer, dimer (C₄F₃H₃), and SiF₄, (from reaction of HF with glass) [45].

A pyrogram for poly(vinylidene fluoride) is shown in Figure 6.3.5. The pyrolysis was done similarly to the PVC, at 600° C in He at a heating rate of 20° C/ms, starting with 0.4 mg sample. The separation was done on a Carbowax column (see Table 4.2.2). The peak identification for the chromatogram shown in Figure 6.3.5 was done using MS spectral library searches, and the results are given in Table 6.3.6.

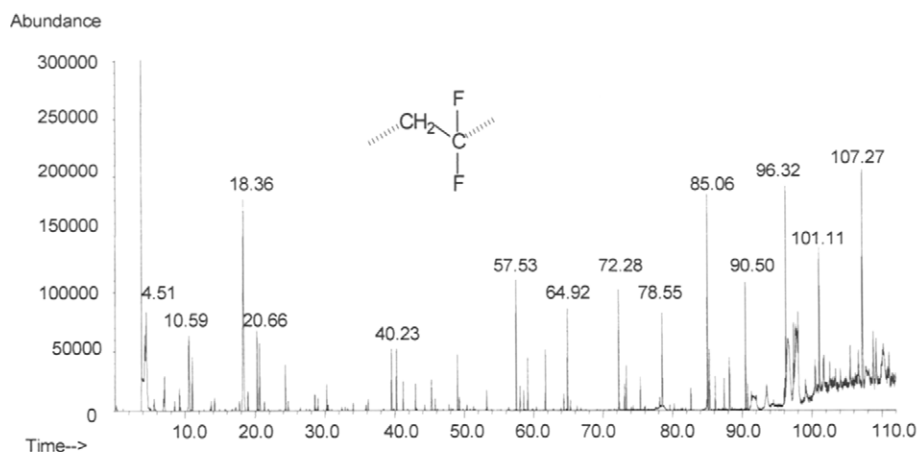


FIGURE 6.3.5. Result for a Py-GC/MS analysis of poly(vinylidene fluoride) $M_w = 180,000$. Pyrolysis done on 0.4 mg material at 600°C in He, with the separation on a Carbowax type column.

TABLE 6.3.6. Compounds identified in the pyrogram of poly(vinylidene fluoride) as shown in Figure 6.3.5.

Peak	Compound	Ret.Time	MW	Area %
1	1-propene	4.23		trace
2	1,1-difluoroethene	4.51	64	7.88
3	2,2,4,4,-tetrafluorobutane	7.08	130	trace
4	1,3,5-trifluorobenzene	10.59	132	5.05
5	3,3,4,4,-tetrafluoro-1,5-hexadiene ?	13.71	154	trace
6	1,4-difluorobenzene	14.23	114	trace
7	water	18.36	18	20.59
8	2,6-difluorotoluene	19.00	128	trace
9	unknown [115(100), 51(43), 46(18), 95(10)]	20.30		3.37
10	1,2,3,4,5-pentafluorocyclohexene	20.66	172	3.22
11	3,3,7,7,7-pentafluoro-1,5-heptadiene	30.23	186	trace
12	1,1,2,2,5,5,6,6-octafluorohexane ?	40.23	230	trace
13	unknown [115(100), 133(60), 51(27), 179(22), 233(14)]	57.53		5.24
14	nonafluoroundecadiene ?	64.92	314	3.77
15	unknown fluorinated polyene	72.28		5.35
16	unknown fluorinated polyene	78.55		4.61
17	unknown fluorinated polyene	85.06		8.71
18	unknown fluorinated polyene	96.32		10.67
19	unknown fluorinated polyene	101.11		7.49
20	unknown fluorinated polyene	107.27		14.04

The identification of the compounds in the pyrolysate of poly(vinylidene fluoride) is difficult because the lighter compounds are not well separated (in the chromatographic conditions used for the sample shown in Figure 6.3.5), and higher molecular mass fluorinated compounds are not common in mass spectral libraries (see also for the identification of mass spectra of fluorinated compounds [46]). The HF generated during the pyrolysis is difficult to detect with GC/MS instrumentation, although up to 62.5% of

the polymer weight can be eliminated as HF. A significant amount of char also is generated in the pyrolysis process. This explains the very low intensity of the pyrogram shown in Figure 6.3.5. The abundance scale in Figure 6.3.5 is 300,000, significantly lower than that for the same quantity (0.4 mg) of other pyrolyzed polymers.

Less common in practice is poly(trifluoroethylene). Poly(trifluoroethylene) behaves during thermal decomposition similarly to poly(vinylidene fluoride). A study on thermal decomposition of this polymer between 380° C and 800° C showed the formation of high yields of HF and of some nonvolatile products [42].

- *Poly(tetrafluoro ethylene) and other poly(perfluorinated alkenes)*

Polytetrafluoroethylene (PTFE), CAS # 9002-84-0, has the formula $(-\text{CF}_2\text{CF}_2-)_n$ and is probably the most common homopolymer obtained from a fluorinated hydrocarbon. PTFE is typically obtained from C_2F_4 at pressure by suspension polymerization in water with free radical initiators. The polymer has many applications due to its excellent heat resistance, electrical insulating properties, and mechanical toughness. The macromolecule of PTFE has very little branching, and the polymer can be found with high crystallinity. The chains of the polymer are rather rigid and do not show a planar zigzag type structure. Thermal degradation starts at about 440° C and is maximum at 540° C [47]. The TGA curve for a PTFE sample is shown in Figure 6.3.6. The heating was done between 30° C and 830° C at a rate of 10° C/min. in air.

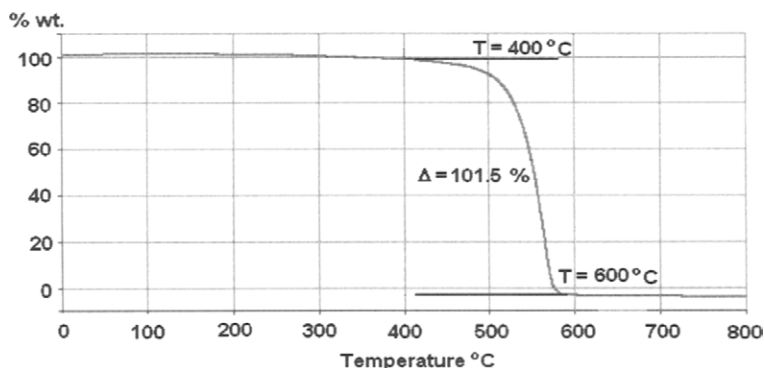


FIGURE 6.3.6. Variation of weight % loss for a PTFE sample in a TGA experiment at a heating rate of 10° C/min.

The polymer generates by thermal degradation a high yield of monomer. Other perfluorinated polyolefins are known in practice. Table 6.3.7 indicates the results of some literature reports regarding the results of thermal decomposition of several perfluorinated polyolefins.

TABLE 6.3.7. Summary regarding literature on thermal decomposition of some perfluorinated polyolefins.

Polymer	Temp. °C	Results	Ref.
poly(tetrafluoro-ethylene)	504–538	about 95% monomer, 2–3% C ₃ F ₆ , no larger fragments (in vacuum)	48
poly(tetrafluoro-ethylene)	1200	monomer yield drops, larger fragments appear (in vacuum)	42
poly(tetrafluoro-ethylene)	600–700	at 6.66 mbar pressure, pure monomer; at 1013 mbar pressure, 15.9% monomer, 25.7% C ₃ F ₆ , 58.4% C ₄ F ₈	49
poly(perfluoro-heptene)	210–270	100% monomer	50
poly(perfluoro-propylene)	280–400	100% monomer	50

The results for a Py-GC/MS analysis of a PTFE sample are shown in Figure 6.3.7. The pyrolysis was done at 600° C in He at a heating rate of 20° C/msec. with 10 sec. THT, starting with 0.4 mg polymer. The separation was done similarly to that for other polymers given previously as examples, on a Carbowax column with the GC starting at 40° C with a ramp of 2° C/min. up to 240° C and a final oven time of 20 min. (see Table 4.2.2).

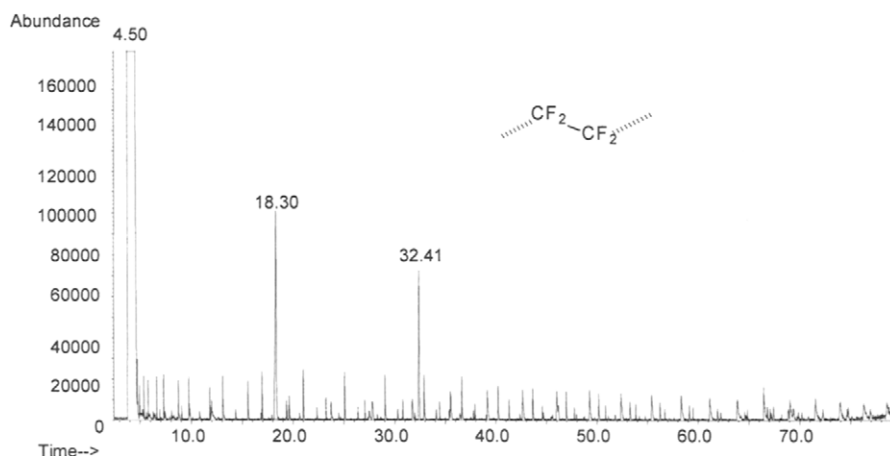


FIGURE 6.3.7. Result for a Py-GC/MS analysis of PTFE. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

The largest peak in the chromatogram of PTFE pyrolysate is that at 4.50 min. This peak is made mainly from C₂F₄ (MW = 100). However, the separation of other perfluorinated hydrocarbons with relatively low MW is not done in the conditions used for the separation (Carbowax column with the GC starting at 40° C). Coeluting with C₂F₄ are traces of hexafluoroethane (MW = 138), octafluoro-1-butene (MW = 200), decafluorobutane (MW = 238), decafluoro-1-pentene (MW = 250), dodecafluoropentane (MW = 288), etc. The chromatogram also contains a large number of small peaks belonging to fragments of either perfluorinated alkanes or perfluorinated alkenes. The

peak at 18.30 min. is water, and the one at 32.41 min. is styrene, both being contaminants and not resulting from PTFE decomposition.

For perfluoropolymers and chlorine-containing fluoropolymers, the depolymerization reaction dominates during pyrolysis. However, the introduction of OCF_3 groups into perfluoropolymers in place of F atoms brings significant changes in their mode of degradation. The OCF_3 groups activate the F atoms attached to the same carbon atoms and make them easier to transfer. Therefore, random chain cleavage accompanied by the F transfer becomes dominant in the course of the pyrolysis. When the F atoms of perfluoropolymers are partly replaced by H atoms, elimination of HF and chain cleavage accompanied by H transfer occur with ease. For fluoropolymers containing H, Cl and OCF_3 as side groups, the depolymerization, the elimination of hydrogen chloride and hydrogen fluoride, and the random chain cleavage accompanied by H and F transfer occur simultaneously and compete with each other [51].

- Other halogenated polyolefins

Several other polymers with saturated carbon chain backbone and halogen side groups were synthesized, such as poly(chlorotrifluoro-ethylene) or KEL-F, CAS# 9002-83-9, poly(1,1-dichloro-2,2-difluoroethylene), and poly(vinyl bromide), CAS# 25951-54-6. Among these, probably KEL-F has more valuable practical applications. KEL-F is used for special packaging, for making seals and gaskets as well as other equipment parts that are chemically resistant, etc. Thermal stability of KEL-F is rather good, the decomposition starting at about 300°C with the formation of monomer and other halocarbon compounds. The polymer can be used at 200°C without obvious modifications of its physical properties.

Much less stable at heating is poly(vinyl bromide), which starts decomposing as low as 100°C with dehydrobromination. Since the dehydrobromination occurs at lower temperatures (activation energy of only 17 kJ mol^{-1}), long chains of unsaturated hydrocarbons are generated and do not decompose until the temperature is further increased. Some literature reports regarding thermal decomposition of these polymers are summarized in Table 6.3.8.

TABLE 6.3.8. Summary of reports regarding the thermal decomposition of poly(chlorotrifluoro-ethylene) or KEL-F, poly(1,1-dichloro-2,2-difluoroethylene), and poly(vinyl bromide)

Polymer	Temp. $^\circ\text{C}$	Results	Ref.
poly(chlorotrifluoro-ethylene) KEL-F	ambient to 500	monomer, traces of dichlorodifluoroethene, chloropentafluoropropene, trichlorotrifluoroethane	52
poly(chlorotrifluoro-ethylene) KEL-F	347-418	25% of products volatile at 25°C monomer with traces of $\text{C}_3\text{F}_5\text{Cl}$ and $\text{C}_3\text{F}_4\text{Cl}_2$; 72.1% of larger chain fragments nonvolatile at 25°C	48
poly(1,1-dichloro-2,2-difluoroethylene)	240	20% black nonvolatile residue; 80% monomer	53
poly(vinyl bromide)	ambient to 500	HBr, ethylene, benzene, and other unidentified minor products	54

A pyrogram for poly(chlorotrifluoroethylene) (KEL-F) is shown in Figure 6.3.8. The pyrolysis was done, similar to other examples previously discussed, at 600° C in He at a heating rate of 20° C/msec. and with separation done on a Carbowax column (see Table 4.2.2).

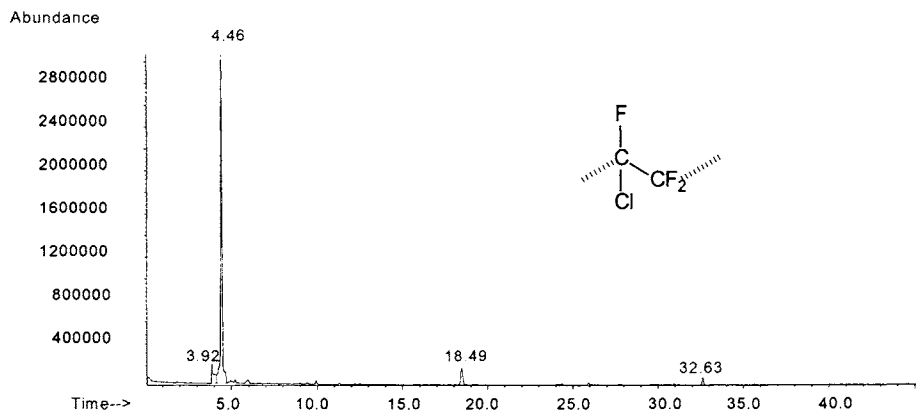
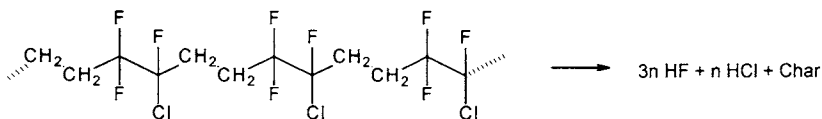


FIGURE 6.3.8. Result for a Py-GC/MS analysis of poly(chlorotrifluoroethylene). Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

As seen from the pyrogram, only very few compounds were generated during pyrolysis at 600° C, the main process during pyrolysis being depolymerization. The monomer chlorotrifluoroethene (MW = 116), eluting in the above-specified conditions at 4.46 min., forms the only compound identified in pyrolysate. Water present in the pyrogram at 18.49 min. is a contamination, and the trace of styrene at 32.63 min. also may come from impurities in the polymer.

Another halogenated polyolefin that contains chlorine and fluorine in the molecule is poly(ethylene-*alt*-chlorotrifluoroethylene), CAS# 25101-45-5. As shown in Section 2.1, the pyrolysis of this polymer takes place with the side chain elimination of HCl and HF by the following reaction:



Besides HF and HCl the pyrolysate of poly(ethylene-*alt*-chlorotrifluoroethylene) still contains a number of fragment molecules. As shown in Figure 6.3.9, the pyrogram for poly(ethylene-*alt*-chlorotrifluoroethylene) is weak, the abundance scale being ten times lower than the one for poly(chlorotrifluoroethylene) shown in Figure 6.3.8. Both pyrograms were obtained from 0.4 mg material in identical conditions, including the same separation. The peak identification for the chromatogram from Figure 6.3.9 is given in Table 6.3.9.

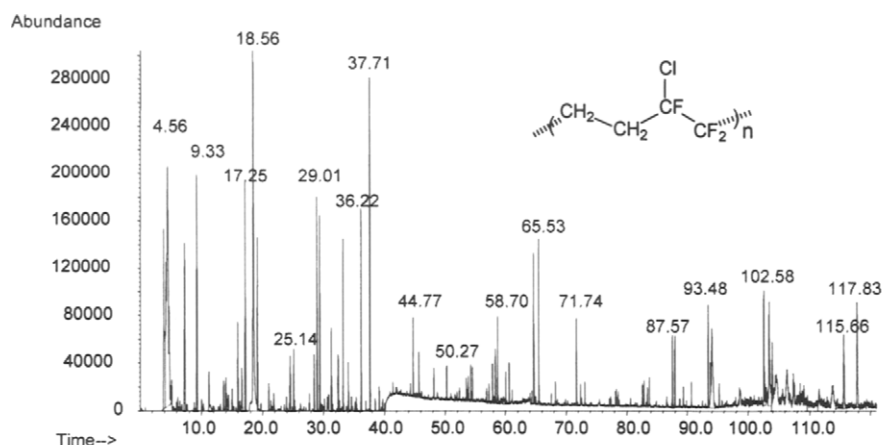


FIGURE 6.3.9. Result for a Py-GC/MS analysis of poly(ethylene-alt-chlorotrifluoroethylene). Pyrolysis done at 600° C, with the separation on a Carbowax type column.

TABLE 6.3.9. Compounds identified in the pyrogram of poly(ethylene-alt-chlorotrifluoroethylene) as shown in Figure 6.3.9.

Peak	Compound	Ret. Time	MW	Area %
1	1,1-difluoroethene	4.45	64	trace
2	chlorotrifluoroethene	4.56	116	28.15
3	1,1,2-trifluoro-2-chloropropane	4.76	132	trace
4	1,1,2,2-tetrafluoropropane	7.34	106	4.70
5	1,1-difluoro-2-chloro-2-propene	9.33	112	5.98
6	hydrochloric acid	12.98	36.5	diffuse peak
7	fluorobenzene	15.06	96	trace
8	chlorotrifluoroethene	16.01	116	trace
9	1,4-difluorobenzene	17.25	114	4.63
10	water + unknown [82(100), 67(89), 69(35), 51(25), 117(23)]	18.56		11.04
11	unknown [82(100), 67(90), 69(36), 51(27), 117(21), 148(8)]	19.23		3.18
12	unknown [77(100), 51(11), 67(6), 69(5)]	29.01		4.08
13	unknown [77(100), 51(12), 67(6), 69(5)]	29.44		3.56
14	unknown [108(100), 119(19), 155(16), 224(13), 169(11)]	33.27		3.11
15	unknown [65(100), 211(9), 175(9), 213(6), 131(6)]	36.22		3.59
16	unknown [77(100), 65(29), 95(4), 111(3), 143(3), 256(2)]	37.71		5.74
17	unknown [77(100), 175(23), 67(17), 131(14), 211(9)]	44.74		1.37
18	unknown [77(100), 67(14), 131(12), 185(10)]	58.73		1.49
19	unknown [65(100), 77(15), 95(14), 127(11), 175(11), 319(8)]	64.70		2.69
20	unknown [77(100), 65(40), 95(6), 143(5), 402(2)]	65.54		3.30
21	unknown	71.74		1.12
22	unknown	87.57		1.17
23	unknown	88.00		1.02
24	unknown [77(100), 115(14), 147(14), 159(14), 185(14), 463(6)]	93.48		2.22
25	unknown [59(100), 45(47), 83(36), 69(28), 381(19)]	94.05		7.86
26	unknown	115.66		3.09
27	unknown	117.83		3.30

Most peaks in the pyrogram of poly(ethylene-*alt*-chlorotrifluoroethylene) remained unidentified. This is typical for fluorinated compounds with higher MW. Also, the pyrogram does not show any peak for HF, although a considerable amount of this compound is generated by pyrolysis. It can be assumed that a small part of the pyrolysate is made from oligomers resulting from the cleavage of the polymer backbone. Others are generated from the cleavage of the polyenes formed by the elimination of the acids and consist of aromatic or unsaturated compounds, some containing residual chlorine and/or fluorine atoms. As expected, some char remains in the pyrolysis tube when this polymer is pyrolyzed.

- Halogenated polyolefins obtained from a preexistent polymer

Polyolefins can be chemically modified with the purpose of changing some of their properties. For example, polyethylene can be chlorinated or chlorosulfonated. Chlorosulfonation can be done with a mixture of chlorine and sulfur dioxide, leading to a material partially chlorinated and partially containing sulfonyl chloride groups. This treatment imparts elastomer character and the capability to be crosslinked, for example, with metallic oxides.

Pyrolysis products of chlorinated polyethylene contain molecules similar to those found in polyethylene pyrolysates and, in addition, compounds similar to that obtained from vinyl chloride (significant amount of HCl). Chlorosulfonated polyethylene typically contains only about 1.5% sulfur, but sulfur-containing compounds such as SO₂ can be detected among its pyrolysis products. The distribution of chlorine atoms in chlorinated polyethylene has been investigated using Py-GC [55, 56]. The polymer was considered equivalent with a terpolymer poly[ethylene-*co*-(vinyl chloride)-*co*-(1,2-dichloroethylene)]. The level of specific degradation products such as aromatic molecules (benzene + toluene + styrene + naphthalene), chlorobenzene, and dichlorobenzenes correlates well with the carbon/chlorine ratio in the polymer.

Another polymer from this group is chlorinated polypropylene. As an example of pyrolysis results for chlorinated polypropylene, the pyrogram of a material containing 32% wt. chlorine (CAS# 68442-33-1) is shown in Figure 6.3.10. The structure of this polymer can be represented by the formula $[-CX(CX_3)CX_2-]_n$, where X = H or Cl. One chlorine per propene unit would lead to approximately 46% wt chlorine. Therefore, the polymer contains slightly less than one chlorine atom per monomer unit. The pyrolysis was done in similar conditions as for other polymers previously presented, namely at 600° C in He at a heating rate of 20° C/msec. and with the separation on a Carbowax column (see Table 4.2.2). The peak identification for the chromatogram from Figure 6.3.10 is given in Table 6.3.10.

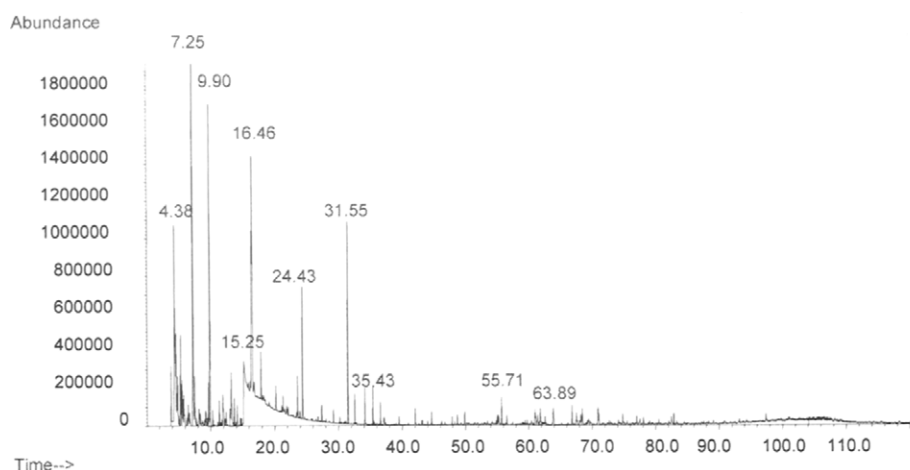
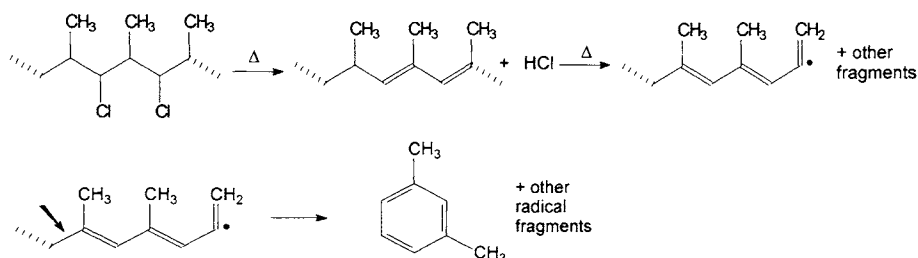


FIGURE 6.3.10. Result for a Py-GC/MS analysis of polypropylene chlorinated with 32% wt. chlorine. Pyrolysis done at 600° C in He, with the separation on a Carbowax type column.

TABLE 6.3.10. Compounds identified in the pyrogram of chlorinated polypropylene 32% wt. chlorine as shown in Figure 6.3.10.

Peak	Compound	Ret. Time	MW	Area%
1	1-propene	4.38	42	6.68
2	2-methyl-1-propene	4.61	56	2.10
3	2-pentene	4.86	70	1.53
4	2-methyl-1-pentene	5.33	84	1.97
5	3,3-dimethyl-1-butene	5.50	84	trace
6	1,4-pentadiene	5.56	68	1.12
7	1,3-pentadiene	5.73	68	0.45
8	2-methyl-1,3-pentadiene	7.25	82	7.93
9	1,3-hexadiene	7.53	82	1.20
10	5,5-dimethyl-1,3-hexadiene	9.73	110	0.90
11	2,4-dimethyl-1-heptene	9.90	126	7.38
12	2,4,6-trimethyl-1-heptene	11.37	140	0.57
13	5,5-dimethyl-1,3-cyclopentadiene	11.95	94	1.14
14	2,4-dimethyl-2,4-heptadiene	13.27	124	1.39
15	6,6-dimethyl-2,4-heptadiene ?	13.72	124	0.60
16	1,2-dimethyl-1,3-cyclopentadiene	14.20	94	0.47
17	HCl (tailed peak, retention time for HCl is not reproducible)	15.25	36	42.49
18	trichloromethane	16.46	118	9.06
19	methylbenzene	17.91	92	0.95
20	1-chloro-1-cyclopropyl-1-propene	20.25	116	0.51
21	unknown [123(100), 83(96), 109(88), 69(69), 82(70)...166(24)]	23.62		0.83
22	1,3-dimethylbenzene	24.43	106	2.62
23	1,2,3-trimethylbenzene	31.55	120	4.08
24	7-methylenetridecane	32.60	196	0.53
25	(1-methylethyl)benzene	34.17	120	0.70
26	unknown [69(100), 85(65), 83(58), 111(56), 84(55) ...154(9)]	35.43	154	0.66
27	unknown [69(100), 85(80), 111(57), 84(55), 83(50) ...154(14)]	36.61	154	0.36
28	2,3-dihydro-4,7-dimethyl-1-indene	55.71	146	0.55
29	unknown [121(100), 43(37), 77(11), 136(5)]	63.89		1.23

By comparing the results for chlorinated polypropylene with those for polypropylene, it can be concluded that the two materials undergo very different pyrolytic reactions. Typical for polypropylene is the formation of fragments of the polymeric backbone with formation of monomer, dimer, etc., or with cleavage of the backbone in random places and formation of compounds with $3n$, $3n-1$, and $3n+1$ carbon atoms (see Section 6.1). Pyrolysis of the chlorinated compound leads to a significant amount of HCl and also char. Very few chlorinated compounds are identified in the pyrolysate, since the elimination of HCl leaves very few chlorine atoms bound to carbons. Some aromatic hydrocarbons are formed by a mechanism similar to that of poly(vinyl chloride) pyrolysis. The elimination of HCl leads to the formation of double bonds, and the breaking of the carbon backbone leads to cyclization and formation of aromatic compounds. The reactions involved in this process are shown below for the case of formation of 1,3-dimethylbenzene:



The formation of aromatic cycles and other radicals can be considered a “bite back” type reaction when the radical reacts with another atom from its own backbone forming cyclic compounds and other radicals.

An interesting case of halogenated polyolefin is that of halogenated poly(vinyl chloride). After-chlorination of PVC improves thermal stability of the polymer. The distribution of chlorine atoms in chlorinated PVC has been studied successfully using Py-GC [57].

- Copolymers of fluorinated and other halogenated olefins

A number of copolymers of halogenated olefins are used in practice. Some of these copolymers are obtained using only fluorinated comonomers. In this group are included poly(vinylidene fluoride-co-perfluoroethylene) CAS# 25684-76-8, poly(vinylidene fluoride-co-hexafluoroisobutene) CAS# 34149-71-8, poly(vinylidene fluoride-co-hexafluoropropene) CAS# 9011-17-0, and the tercopolymer poly(vinylidene fluoride-co-hexafluoropropene-co-tetrafluoroethylene) CAS# 25190-89-0. Some of these copolymers are used in high performance greases and engine oils (when they have lower DP), chemically resistant coatings, temperature and solvent resistant gaskets and hoses, etc. Other copolymers have chlorine atoms besides fluorine attached to the carbon chain, such as poly(1,1-difluoroethene-co-chlorotrifluoroethene), and even oxygen containing groups like poly[tetrafluoroethene-co-trifluoro(trifluoromethoxy)ethene]. Poly(1,1-difluoroethene-co-chlorotrifluoroethene) is used in lacquers, paints, lubricants, adhesives, leather substitutes, etc. and has a special application for plastic-bonded explosives and propellants.

The thermal stability of these copolymers is the highest for the perfluorinated copolymers and decreases with the presence of hydrogens, chlorine, or other groups different from fluorine. For example, poly(vinylidene fluoride-co-hexafluoroisobutene) 50/50 copolymer shows in N₂ a weight loss of 0.03% at 350° C, 0.22% at 400° C and 53% at 500° C. Thermal degradation of poly(1,1-difluoroethene-co-chlorotrifluoroethene) starts at temperatures lower than 400° C [58]. Hydrogen halide gases are liberated above 230° C [59, 60]. The decomposition is more rapid when the chlorine content is higher. Pyrolysis of poly(1,1-difluoroethene-co-chlorotrifluoro-ethene) takes place with elimination of HF and chain cleavage accompanied by H-transfers. Major pyrolysis products include HF, HCl, CF₂=CH₂, CF₂=CFCl, C₃F₅Cl, HCl, C₃F₅H₃, C₃F₄H₃Cl, C₅F₆H, etc. [61]. Thermal decomposition of other fluorinated copolymers is also reported in literature [61–64], etc.

Poly[tetrafluoroethene-co-trifluoro(trifluoromethoxy)ethene] also decomposes at lower temperatures than perfluorinated macromolecules, and the major products of pyrolysis include hydrogen fluoride [65], tetrafluoroethene, hexafluoroethane and perfluoro(methyl vinyl) ether [64].

Some other reported results for thermal decomposition of copolymers of fluorinated and other halogenated olefins are indicated in Table 6.3 11.

TABLE 6.3.11. *Summary of reports regarding the thermal decomposition of copolymers of fluorinated and other halogenated olefins [19].*

Polymer	Temp. °C	Results	Ref.
poly(ethylene-co-chlorotrifluoroethylene)	590	C ₂ H ₄ , CH ₂ =CF ₂ , C ₂ F ₃ H, C ₂ FH ₃ , CF ₂ =CFCl, CH ₂ =CFCl main pyrolysis products	61
poly(ethylene-co-tetrafluoroethylene-co-nonafluorobutylethylene)	650	various oligomers; oligomer ratio allows the determination of copolymer composition	66
poly(methyl methacrylate-co-chlorotrifluoroethylene) 7.7 mol% MMA	ambient to 500	HCl, CO ₂ , CH ₃ Cl, C ₂ F ₃ Cl (monomer), C ₃ F ₅ Cl, C ₂ F ₃ Cl ₃ , methyl methacrylate, chain fragments possibly with some lactonization	67
poly(methyl methacrylate-co-chlorotrifluoroethylene) 77.7, and 85.7 mol % MMA	ambient to 500	HCl, CO ₂ , CH ₃ Cl, C ₂ F ₃ Cl (monomer), methyl methacrylate	67
poly(tetrafluoroethylene-co-hexafluoropropylene)	590	C ₂ F ₄ , CF ₃ -CF=CF ₂ main pyrolysis products	51
poly(vinyl acetate-co-vinyl fluoride) 80/20 to 23/77	200-500	HF, HCl, hydrocarbons	68
poly(vinyl acetate-co-vinyl fluoride) 91/9 to 1/89	200-500	HF, acetic acid, hydrocarbons	68
poly(vinylidene fluoride-co-chlorotrifluoroethylene) 80 mol% VDF	ambient to 500	HCl, HF, vinylidene fluoride, chlorotrifluoroethylene, dimer (C ₄ F ₃ H ₃)	45
poly(vinylidene fluoride-co-hexafluoropropylene)	590	C ₂ F ₄ , CF ₂ =CFCl C ₃ F ₅ Cl main pyrolysis products	61
poly(vinylidene fluoride-co-perfluoroethylene)	?	HF, fluorinated hydrocarbons	69
poly(vinylidene fluoride-co-tetrafluoroethylene-co-hexafluoropropylene)		C ₂ F ₄ , CF ₂ =CH ₂ , CF ₃ -CF=CH ₂ main pyrolysis products	61

An example of a TGA curve for a poly(vinylidene fluoride-co-hexafluoro-propylene), CAS# 9011-17-0, sample is shown in Figure 6.3.11. The heating was done between 30° C and 830° C at a rate of 10° C/min. in air.

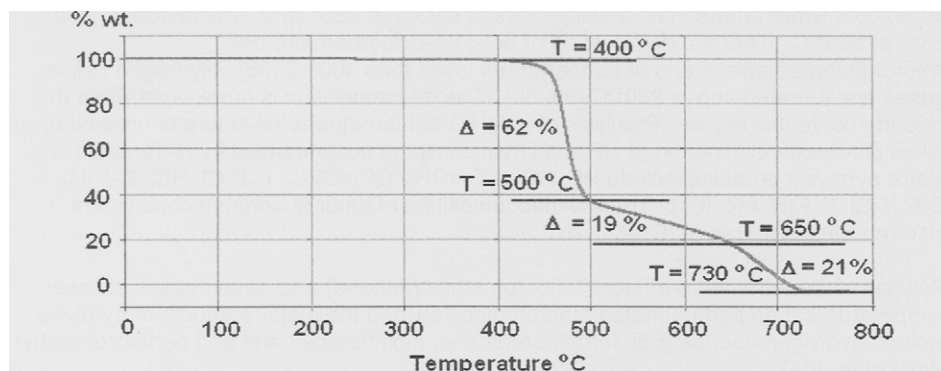


FIGURE 6.3.11. Variation of weight % loss for a poly(vinylidene fluoride-co-hexafluoro-propylene) sample in a TGA experiment at a heating rate of 10° C/min.

Three distinct regions can be seen in the TGA profile. They correspond to complex processes. The HF elimination alone cannot account for 62 % weight loss. The content of HF by weight in the homopolymer poly(vinylidene fluoride) is about 62.5%, and the loss seen in the TGA would indicate no poly(hexafluoropropylene). However, this is not the case.

A pyrogram for poly(vinylidene fluoride-co-hexafluoro-propylene) is shown in Figure 6.3.12. The copolymer has $M_w = 455,000$ and has the idealized formula $(-\text{CH}_2\text{CF}_2)_x [-\text{CF}_2\text{CF}(\text{CF}_3)]_y$. The pyrolysis was done similarly to that of PVC (see Table 4.2.2).

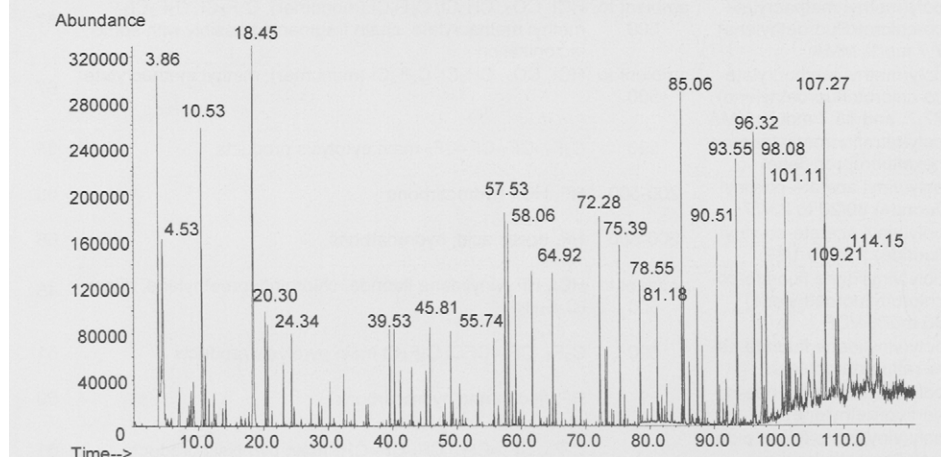


FIGURE 6.3.12. Result for a Py-GC/MS analysis of poly(vinylidene fluoride-co-hexafluoro-propylene), $M_w = 455,000$. Pyrolysis done at 600° C in He, with the separation on a Carbowax type column.

The peak intensities in the pyrogram are in general low compared to other pyrograms, mainly of nonhalogenated macromolecules. Air (ret. time 3.86) and water (ret. time 18.45) appear as large peaks, although their areas are not higher than those for other polymer pyrolysates. A few fluorinated compounds such as 1,1-difluoro-ethene (MW = 64), hexafluoropropene (MW = 150), 1,1,2,2-tetrafluoropropane (MW = 116), 2,2,3,3-tetrafluorobutane (MW = 130), 1,3,5-trifluorobenzene (MW = 132), and 3,3,4,4-tetrafluoro-1,5-hexadiene (MW = 154) can be identified using mass spectral library searches. Other peaks belong to fluorinated compounds with higher MW, but their identification is uncertain. Similarly to the case of PTFE, the fluorinated compounds are not well separated on the Carbowax column. The molecular weight of the compounds in the pyrogram increases very rapidly with the retention time, since fluorinated compounds are non-polar and poorly retained by the column. The identification of these compounds by their mass spectra is very difficult, and most peaks in the pyrogram remained unidentified.

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6.4 HALOGENATED POLYSTYRENES

- General aspects

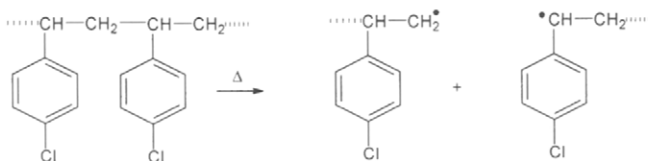
A number of halogenated polystyrenes are used in practice, either for specific applications as thermoplastics or in copolymers. Among the halogenated polystyrenes, the most common are the poly(chlorostyrenes). Poly(4-chlorostyrene) can be obtained in isotactic form (CAS# 24991-47-7) or in syndiotactic form (CAS# 62319-29-3) and is represented by the formula $[-CH_2CH(p-C_6H_4Cl)]_n$. Other poly(chlorostyrenes) include poly(2-chlorostyrene) with CAS# 26125-41-7, and poly(3-chlorostyrene) with CAS# 26100-04-9, CAS#116002-24-5 (isotactic), and CAS# 107830-48-8 (syndiotactic).

A different chlorinated polystyrene is indicated in literature [1] as poly(chlorostyrene), CAS# 9022-52-0. Halogenated polystyrenes also include poly(*p*-chloro- α -methylstyrene), poly[*p*-(2,4-dichlorobenzyl)-styrene], etc. Thermal degradation, not necessarily by flash pyrolysis, has been studied and reported for a number of halogenated polystyrenes [2, 3], and poly(α -methylstyrenes). Some of these reports are summarized in Table 6.4.1 [1].

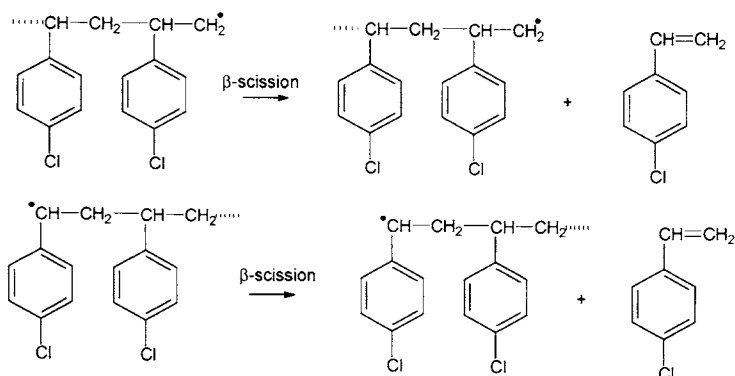
TABLE 6.4.1. Summary of reports regarding the thermal decomposition of various halogenated polystyrenes.

Polymer	Temp. °C	Results	Ref.
poly(2,3,4,5,6-pentafluorostyrene)	390–446	63% of the products are volatile at 25° C, contains some monomer	4
poly(α,β,β -trifluorostyrene)	333–382	72% monomer, 28% larger chain fragments	5
poly(<i>p</i> -chloromethylstyrene)	ambient to 560	two stages are observed, the first beginning at 285° C finished at 400° C with about 40% loss, and the second continuing to up to 70% weight loss; in the first stage the main thermal degradation products are HCl and monomer; isothermal rates based on random initiation generate good agreement with the experiment following the equation $d\alpha/dt = k(1-\alpha)$ (α = conversion); activation energy is 39.6 kcal mol ⁻¹ , and $A = 6.24 \cdot 10^{12}$ min ⁻¹ .	6
poly(styrene) chain brominated on α -position	150–300	HBr, trace styrene	7
poly(styrene) chain brominated on α -position	300–500	styrene, HBr, toluene, benzene	7
poly(styrene) chain brominated on α -position	ambient to 500	HBr, styrene, traces of toluene and benzene, <i>p</i> -bromostyrene	8
poly[4-(3-chloropropyl)-styrene]	500	depolymerization similar to that of polystyrene	9
poly[<i>p</i> -(2,4-dichlorobenzyl)-styrene]	ambient to 500	benzene, toluene, ethylbenzene, styrene, α -methylstyrene, 1,3-dichlorobenzene, 2,4-dichlorotoluene, monomer (major product), complex series of halogenated and dehalogenated chain fragments	10

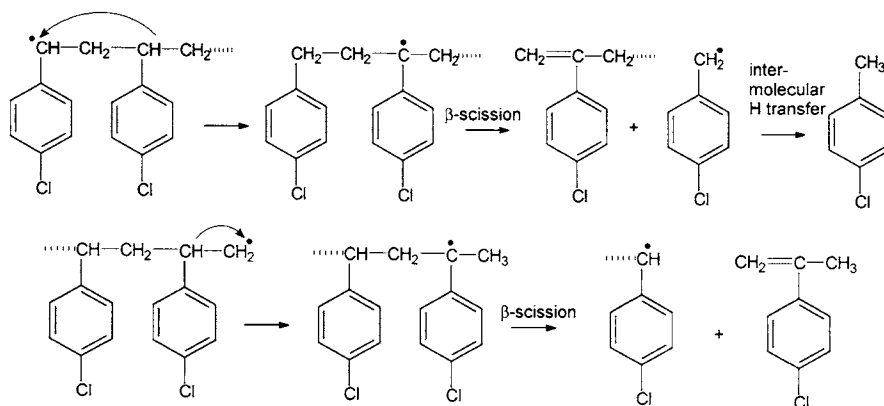
Polymers containing a halogen attached to a carbon in α -position to another aliphatic carbon-bearing hydrogen(s) eliminate very easily the hydrohalogenated acid. This is not the case for halogens bound to an aromatic ring. Poly(4-chlorostyrene) has reasonably good thermal stability, starting to decompose at about 400–420° C [11, 12]. The chlorinated benzene ring influences the stability of the carbon chain backbone more strongly than a simple benzene ring, and the yield of monomer during the thermal decomposition of poly(*p*-chlorostyrene) is higher than that for styrene. It is likely that the thermal decomposition starts with a random chain scission as shown below:



The radical formed in the reaction will generate the monomer by β -scissions:



The β -scission is favored compared to other scissions by the strong effect of p-chlorobenzene group. Other reactions likely to occur during the pyrolysis are due to hydrogen transfer reactions followed again by β -scissions as shown in the following schemes:



The results for a Py-GC/MS analysis of a sample of poly(4-chlorostyrene) are shown in Figure 6.4.1. The pyrolysis was done at 600° C in He at a heating rate of 20° C/msec. The separation was done on a Carbowax column (60 m, 0.32 mm i.d., 0.32 μm film thickness) with the GC starting at 40° C with a ramp of 2° C/min. up to 240° C and a final oven time of 20 min. (see Table 4.2.2). The MS was operated in EI+ mode. The peak identification for the chromatogram from Figure 6.4 1 is given in Table 6.4.2.

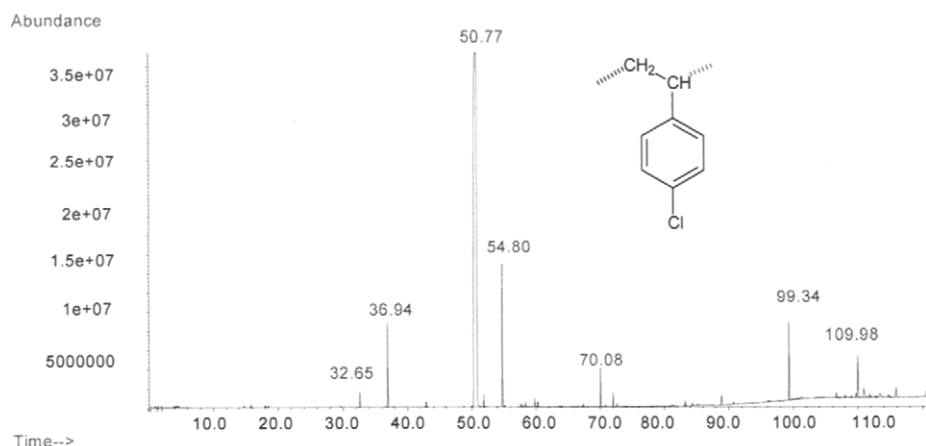


FIGURE 6.4.1. Result for a Py-GC/MS analysis of poly(*p*-chlorostyrene). Pyrolysis done at 600° C in He, with the separation on a Carbowax type column.

TABLE 6.4.2. Compounds identified in the pyrogram of poly(*p*-chlorostyrene) as shown in Figure 6.4.1.

Peak	Compound	Ret. Time	MW	Area %
1	toluene	18.02	92	trace
2	water	18.50	18	trace
3	chlorobenzene	29.73	112	trace
4	styrene	32.65	104	0.58
5	1-chloro-4-methylbenzene	36.94	126	3.34
6	1-methylethenylbenzene	37.50	118	trace
7	1-chloro-4-ethylbenzene	42.92	140	0.21
8	1-chloro-2(1-methylethyl)benzene	45.80	154	trace
9	1-chloro-2-propylbenzene	48.57	154	trace
10	1-chloro-2-ethenylbenzene	48.88	138	trace
11	1-chloro-4-ethenylbenzene (<i>p</i> -chlorostyrene)	50.77	138	78.51
12	1-chloro-4-propenylbenzene	51.89	152	0.44
13	4-chloro- α -methylstyrene	54.80	152	5.75
14	1-chloro-4-(1-methylenepropyl)benzene	57.64	166	0.13
15	2-chloro-1-allylbenzene	59.83	152	0.35
16	1,4-dichloro-2-ethenylbenzene	60.29	172	0.22
17	naphthalene	63.74	128	trace
18	4-chlorobenzaldehyde	65.42	140	trace
19	1,1-dichloroethylbenzene	67.38	174	0.16
20	1-methylnaphthalene	70.08	142	1.54
21	2-methylnaphthalene	72.03	142	0.63
22	1-(4-chlorophenyl)buta-1,3-diene	72.38	164	trace
23	1,2-dichloro-4-(1-methylethenyl)benzene	81.16	186	trace
24	4-chloro- α -methylbenzenemethanol	84.38	156	0.13
25	unknown [125(100), 127(33), 193(12)]	88.88		0.39
26	unknown [115(100), 116(86), 152(72), 219(42)]	99.34		3.18
27	1,1'-methylenebis(4-chlorobenzene)	109.60	236	trace
28	1-chloro-4-[1-benzylvinyl]benzene	109.98	228	2.39
29	1,1'-ethenylidenebis(4-chlorobenzene)	110.88	248	0.77
30	4-chloro-1-[(2-(4-chlorophenyl)propyl)benzene]	115.86	250	0.72
31	1[2-(4-chlorophenyl)-1-methylprop-1-enyl]-4-chlorobenzene	120.57	276	0.53

Similar pyrolysis products with poly(4-chlorostyrene) are obtained from the pyrolysis of poly(4-bromostyrene), CAS# 24936-50-3, [13]. The main compounds identified in the pyrogram of poly(*p*-bromostyrene) are given in Table 6.4.3.

TABLE 6.4.3. *Compounds identified in the pyrogram of poly(p-bromostyrene) [13].*

Peak	Compound	MW	Weight %
1	light hydrocarbons		0.44
2	2-methylpropenenitrile	67	0.17
3	2-methylpropanenitrile	69	0.62
4	benzene	78	0.01
5	toluene	92	0.04
6	ethylbenzene	106	0.01
7	styrene	104	0.27
8	bromobenzene	157	0.46
9	α -methylstyrene	118	0.07
10	indane	118	0.04
11	<i>o</i> -bromotoluene	171	0.09
12	<i>p</i> -bromotoluene	171	9.75
13	bromoethylbenzene	185	2.50
14	<i>o</i> -bromostyrene	183	0.55
15	1-bromo-4-ethenylbenzene (<i>p</i> -bromostyrene)	183	73.64
16	bromoisopropylbenzene	199	0.08
17	1- <i>p</i> -bromophenylpropene	197	0.13
18	bromopropylbenzene	199	0.07
19	2- <i>p</i> -bromophenylpropene	197	2.20
20	C ₉ H ₉ Br	197	0.04
21	bromindane	197	0.72
22	bromoindene	195	0.02
23	bromonaphthalene	207	0.42
24	cyanoisopropylbromotoluene (initiator)	238	0.03
25	bromomethylnaphthalene	221	0.17
26	C ₁₂ H ₉ Br (bromobiphenyl)	233	0.03
27	cyanoisopropylbromoethylbenzene (initiator)	252	0.09
28	cyanoisopropylbromostyrene (initiator)	250	0.02
29	cyanoisopropyl- <i>p</i> -bromophenylpropene (initiator)	264	0.17
30	C ₁₄ H ₁₃ Br (bromodiphenylethane)	261	0.02
31	C ₁₅ H ₁₃ Br (bromodiphenylpropene)	273	0.09
32	C ₁₃ H ₁₀ Br ₂ (di- <i>p</i> -bromophenylmethane)	326	0.22
33	C ₁₄ H ₁₀ Br ₂ (di- <i>p</i> -bromophenylethane)	338	0.33
34	C ₁₄ H ₁₂ Br ₂ (di- <i>p</i> -bromophenylethane)	340	0.42
35	C ₁₆ H ₁₄ Br ₂	366	0.33
36	1,3-di- <i>p</i> -bromophenylpropane	354	0.91
37	<i>p</i> -bromostyrene dimer	366	1.50
38	C ₁₄ H ₁₀ Br ₂	338	0.08
39	di- <i>p</i> -bromophenylpropene	352	0.51
40	C ₁₆ H ₁₄ Br ₂	366	0.46
41	C ₁₆ H ₁₂ Br ₂ (dibromophenylbutadiene)	364	0.19
42	C ₁₇ H ₁₄ Br ₂	378	0.04
43	dibromophenylnaphthalene	362	0.15
44	dibromobenzylnaphthalene	376	0.18

As seen in Table 6.4.3, the brominated molecules resulting from the brominated polystyrene represent more than 96% of the pyrolysis products. However, a small proportion of hydrocarbons characteristic for poly(styrene) pyrolysis are present. These

compounds indicate that a small proportion of unbrominated styrene units are present in the polymer sample that was pyrolyzed. Also, a number of cyanopropyl derivatives are seen in the pyrolysate (comprising about 1% of the material). The polymer used as a sample for pyrolysis in the reported study [13] was obtained from p-bromostyrene polymerization in the presence of α, α' -azobisisobutyronitrile as initiator. The small amount of initiator present in the polymer explains the presence of these nitrogen-containing compounds. Poly(4-fluorostyrene), CAS# 24936-47-8, and poly(4-iodostyrene), CAS# 24936-53-6, also are known, but no pyrolysis studies are available.

Another chlorinated derivative of polystyrene is poly(vinyl benzyl chloride), CAS# 121961-20-4, with the formula $[-CH_2CH(C_6H_4CH_2Cl)]_n$. This polymer is a mixture of 3- and 4- isomers in 60/40 ratio. The results for a Py-GC/MS analysis of a sample with $M_w = 100,000$ are shown in Figure 6.4.2. The pyrolysis was done at 600° C in He at a heating rate of 20° C/msec. with 10 sec. THT. The separation was done similarly to that for other polymers given previously as examples, on a Carbowax column with the GC starting at 40° C with a ramp of 2° C/min. up to 240° C and a final oven time of 20 min. (see Table 4.2.2).

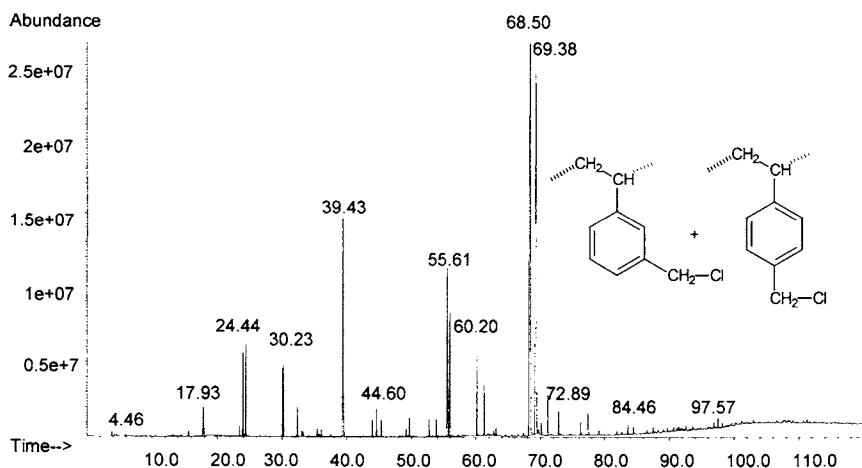


FIGURE 6.4.2. Result for a Py-GC/MS analysis of poly(vinyl benzyl chloride) $M_w = 100,000$ (mixture of 3- and 4- isomers in 60/40 ratio). Pyrolysis done on 0.4 mg material at 600° C, with the separation on a Carbowax type column.

The peak identification for the chromatogram shown in Figure 6.4.2 was done using MS spectral library searches only and is given in Table 6.4.4.

TABLE 6.4.4. Compounds identified in the pyrogram of poly(vinyl benzyl chloride) (mixture of 3- and 4- isomers in 60/40 ratio) as shown in Figure 6.4.2.

Peak	Compound	Ret Time	MW	Area %
1	propene	4.46	42	trace
2	chloromethane	4.90	50	trace
3	acetaldehyde	5.95	44	trace
4	hydrochloric acid	12.98	36	diffuse peak
5	2-methylpropanenitrile	15.62	69	trace
6	methylbenzene	17.93	92	1.35
7	ethylbenzene	23.48	106	0.30
8	1,4-dimethylbenzene	23.99	106	2.46
9	1,3-dimethylbenzene	24.44	106	2.73
10	1-ethyl-2-methylbenzene	30.09	120	3.36
11	1-ethyl-3-methylbenzene	30.23	120	4.16
12	styrene	32.39	104	0.81
13	1-methyl-2(1-methylethyl)benzene	33.06	134	trace
14	1,3-diethylbenzene	35.46	134	0.36
15	1,2-diethylbenzene	36.11	134	0.20
16	1-ethenyl-3-methylbenzene	39.43	118	10.50
17	methyl(1-methylethenyl)benzene	43.97	132	0.50
18	1-methyl-3-(2-propenyl)benzene	44.60	132	0.96
19	1-ethenyl-4-ethylbenzene	45.33	132	0.53
20	2-ethenyl-1,4-dimethylbenzene	49.19	132	0.39
21	(chloromethyl)benzene	49.69	126	0.58
22	1,3-diethenylbenzene	52.75	130	0.49
23	1,4-diethenylbenzene	53.87	130	0.53
24	1-(chloromethyl)-3-methylbenzene	55.61	140	5.69
25	1-(chloromethyl)-4-methylbenzene	56.00	140	3.81
26	1-(chloromethyl)-3-ethylbenzene	60.20	154	2.59
27	1-(chloromethyl)-4-ethylbenzene	61.32	154	1.56
28	1-chloro-1-phenyl-1-propene	63.17	152	0.32
29	1-(chloromethyl)-3-ethenylbenzene	68.50	152	28.15
30	1-(chloromethyl)-4-ethenylbenzene	69.38	152	22.67
31	3-phenyl-2-propenal ?	70.18	132	0.50
32	isopropenyl-3-(α -chlorotoluene)	71.19	166	1.20
33	isopropenyl-4-(α -chlorotoluene)	72.89	166	0.68
34	1-allyl-4-chlorobenzene	76.29	166	0.42
35	1,2-dichloro-2,3-dihydro-1H-indene	77.39	186	1.02
36	(1,2-dichloroethyl)-toluene	77.44	188	trace
37	1,3-dichloro-2,3-dihydro-1H-indene	79.12	186	trace
38	2-ethenyl-naphthalene	81.90	154	trace
39	1,3-bis(chloromethyl)benzene	83.62	186	0.26
40	1,4-bis(chloromethyl)benzene	84.46	186	0.31
41	1,1'-(1,3-ethandiyl)bis(4-methyl)benzene	90.70	210	trace
42	1,3-bis(4-methylphenyl)propane	96.91	224	0.32
43	1,3-bis(3-methylphenyl)propane	97.57	224	0.30

The pyrogram of poly(vinyl benzyl chloride) is very similar to that of other polystyrene related polymers. The presence of two main monomer peaks in the pyrogram is caused by the fact that the polymer is a mixture of 3 and 4 substituted polymer. The peak area ratios of several 3- and 4-isomers is around 60/40. For example, for 1-(chloromethyl)-3-methylbenzene and 1-(chloromethyl)-4-methylbenzene the ratio is 59.9/40.1, for 1-(chloromethyl)-3-ethylbenzene and 1-(chloromethyl)-4-ethylbenzene the ratio is

62.4/37.6, and for 1-(chloromethyl)-3-ethenylbenzene and 1-(chloromethyl)-3-ethenylbenzene the ratio is 55.4/44.6. This shows that the ratio of the pyrolysis products is very close to that of the polymers, and the decomposition of the two polymers does not occur differently. The cleavage of the carbon backbone of the polymer, being associated with some hydrogen migration, will generate some isopropenyl-(α -chlorotoluene) and some 1-(chloromethyl)-3- or -4-methyl-benzene, which are the equivalents of isopropenylbenzene and toluene in PS pyrolysate.

- Copolymers of halogenated styrenes

Halogenated styrenes can form a number of copolymers, some used in blends with polystyrenes or other polymers. Examples of such copolymers are poly(*o*-chloro-styrene-*co-p*-chlorostyrene), polystyrene-*co*-poly(2-chlorostyrene) [14], poly(methyl acrylate-*co*-4-chlorostyrene), etc. A few studies on thermal behavior of these polymers are available [15, 16].

Several studies of pyrolysis of chlorostyrene copolymers were reported in literature. One of these studies evaluates the sequence distribution of dyads in styrene-*m*-chlorostyrene copolymer and in styrene-*p*-chlorostyrene copolymer [17]. The results are obtained using data from pyrolysis performed at 550° C and FID detection. In a similar study, the sequence distribution of dyads was evaluated for poly(acrylonitrile-*co-m*-chlorostyrene) and for poly(acrylonitrile-*co-p*-chlorostyrene) [18] (see also Section 4.3).

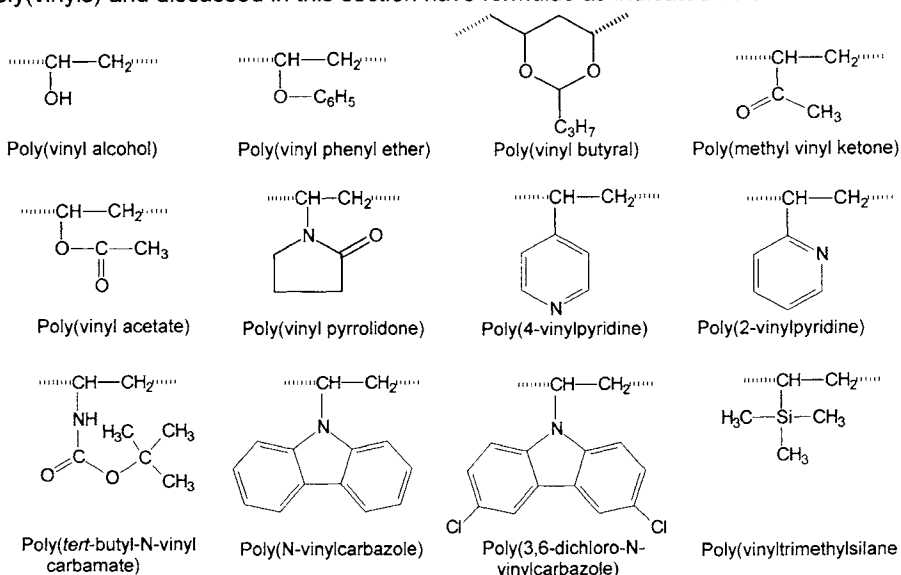
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6.5 POLY(VINYLS) WITH -OH, -O-R, -OC(O)-R, -C(O)-R, -C₅H₄N, AND OTHER SUBSTITUENTS

- General aspects

Poly(vinyls) substituted with -OH, -O-R, -OC(O)-R, -C(O)-R, -C₅H₄N, etc. groups form one important class of synthetic polymers having saturated carbon chain backbone. Other polymers derived from the vinyl group with specific substituents such as poly(halogenated olefins), poly(styrenes), poly(acrylates), and poly(methacrylates) form their own classes and are not included here. Examples of polymers known as poly(vinyls) and discussed in this section have formulas as indicated below:



The decomposition mechanism during flash pyrolysis of the compounds from this class depends considerably on the nature of the substituent at the carbon backbone. Some polymers suffer elimination of the side group similar, for example, to poly(vinyl chloride), followed by the breaking of the carbon chain containing double bonds. Other molecules suffer reactions at the side chain groups without side group elimination, an example being poly(vinyl methyl ketone), which undergoes an aldol condensation between two adjacent side groups. For other polymers the main reaction is the cleavage of the carbon backbone before other reactions. In many cases, pyrolysis occurs as a complex process with simultaneous participation of the side groups as well as with the cleavage of the carbon chain backbone.

- Poly(vinyl alcohol)

Poly(vinyl alcohol) (PVA), CAS# 9002-89-5, is a polymer with numerous practical applications, being water soluble and also soluble in several other solvents such as alcohol/water mixtures, glycols, glycerin (hot), etc. Because PVA is nontoxic and

biodegradable, it is used in cosmetics and for some medical applications. It is used in adhesives, coatings, emulsion stabilizers, in paper industry, as a carrier polymer in inks, in textile industry as a sizing agent, in fiber manufacturing, and as an intermediate material for the synthesis of other polymers such as poly(vinyl acetals). Specific derivatizations can be applied to produce materials with practical applications. One such derivatization is done using formaldehyde in the presence of Na_2SO_4 and H_2SO_4 to form an acetal that is insoluble in water. The procedure is applied on poly(vinyl alcohol) fibers that retain some of the OH groups and maintain hydrophilic character although they do not remain water soluble. This type of fiber can be used as a cotton replacement. Another acetal of polyvinyl alcohol that has practical applications is poly(vinyl butyral), which is used, for example, for making safety glass laminates.

Poly(vinyl alcohol) is typically obtained by alcoholysis of poly(vinyl esters), for example from poly(vinyl acetate) and methanol in the presence of NaOH. The process can be completed or only partially conducted. In this latter case a copolymer (alcohol/ester) is obtained. Other synthetic procedures are used, most of them also based on the hydrolysis of poly(vinyl esters). Poly(vinyl alcohol) is typically used in the atactic form, but isotactic or syndiotactic poly(vinyl alcohols) also are known.

A significant number of studies have been dedicated to the evaluation of poly(vinyl alcohol) thermal stability [1–8]. The TG curve for a poly(vinyl alcohol) sample with $M_w = 89,000$ – $98,000$ is shown in Figure 6.5.1. The heating was done in air between 30°C and 830°C at a rate of 10°C/min .

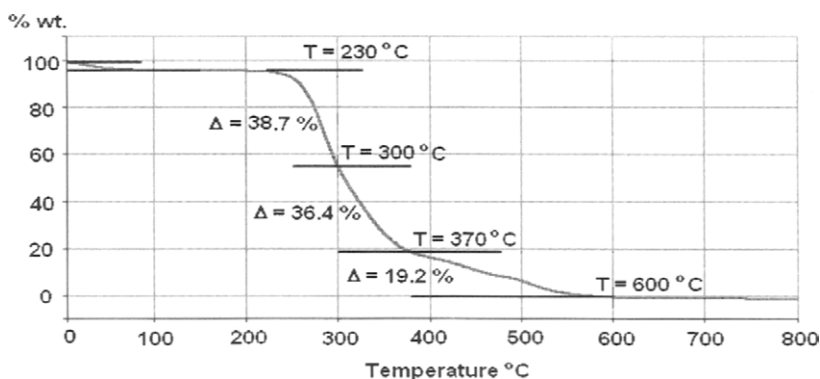


FIGURE 6.5.1. Variation of weight % loss for a poly(vinyl alcohol) sample in a TGA experiment at a heating rate of 10°C/min .

The first step in the TG curve (3.4% weight loss) is probably due to the loss of adsorbed water. The decomposition continues with a rather complex profile. The loss of one water molecule per monomer unit corresponds to 40.91% weight loss, which is relatively close to the lost weight in the second step of the TG curve from Figure 6.5.1 of about 39% (37.7% corrected for initial loss of adsorbed water). This would suggest that PVA pyrolysis starts with the elimination of a water molecule. However, the complete elimination of water would allow only further formation of hydrocarbons and char in the next steps of decomposition. This is not confirmed by the results provided by the

analysis of pyrolysates that do contain hydrocarbons but also considerable levels of aldehydes and ketones. Moreover, the decomposition of PVA may depend on the manufacturing conditions of the polymer. In the presence of oxygen, the oxidation of the unsaturated polymeric residue leads to the formation of a higher content of carbonyl compounds. Some degradation products of PVA reported in literature indicate a quantitative removal of water at 250° C [9] and in a different report [10] formation of H₂O and C₂H₅OH, aldehydes and ketones e.g. CH₃-(CH=CH)_n-CHO CH₃-(CH=CH)_n-COCH₃ where n= 0,1,2, etc. at 240° C. Other studies on PVA pyrolysis also are published [11].

Results for a Py-GC/MS analysis of a PVA sample with M_w = 89,000–98,000 are shown in Figure 6.5.2. The pyrolysis was done at 600° C in He at a heating rate of 20° C/ms. with 10 s THT. The separation was done similarly to that for other polymers given previously as examples, on a Carbowax column with the GC starting at 40° C with a ramp of 2° C/min. up to 240° C and a final oven time of 20 min. (see Table 4.2.2). The peak identification for the chromatogram shown in Figure 6.5.2 was done using MS spectral library searches and is given in Table 6.5.1.

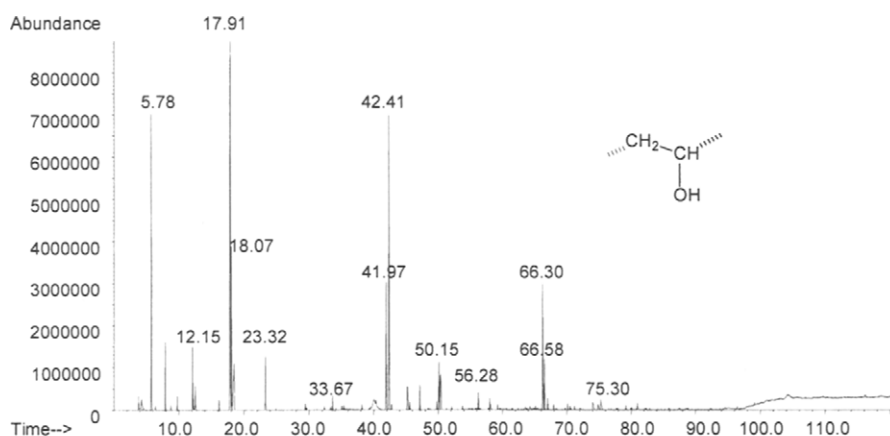


FIGURE 6.5.2. Result for a Py-GC/MS analysis of poly(vinyl alcohol) M_w = 89,000–98,000. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 6.5.1. Compounds identified in the pyrogram of poly(vinyl alcohol) as shown in Figure 6.5.2.

Peak	Compound	Ret. Time	MW	Area %
1	acetaldehyde	5.78	44	12.26
2	cyclopentadiene	6.42	66	trace
3	propanone	7.96	58	2.26
4	propenal	8.81	56	trace
5	butanal	9.79	72	0.52
6	2,5-dihydrofuran	12.15	70	2.20
7	ethanol	12.28	46	0.50
8	benzene	12.56	78	0.87
9	2,3-dihydro-3-methylfuran	16.21	84	0.43
10	2-butenal	17.91	70	22.86

TABLE 6.5.1 (continued). Compounds identified in the pyrogram of poly(vinyl alcohol) as shown in Figure 6.5.2.

Peak	Compound	Ret. Time	MW	Area %
11	2-methyl-2-propenal	18.07	70	6.53
12	water	18.55	18	4.68
13	3-methyl-3-buten-2-one	23.32	84	2.11
14	2-buten-1-ol	29.48	72	0.41
15	2-methylene-2-pentenal	33.67	96	0.61
16	1,5-dimethylcyclopentene ?	40.07	96	1.87
17	2-ethylfuran	41.97	96	6.13
18	(E,E)-2,4-hexadienal	42.41	96	15.24
19	acetic acid	45.24	60	1.80
20	2,2-dimethyl-4-cyclopenten-1-one	45.60	110	0.43
21	4,4-dimethyl-2-cyclopenten-1-one	47.19	110	1.07
22	1,3-bis(methylene)cyclohexane ?	49.81	108	0.58
23	2,4,6-octatrienal	50.15	122	2.31
24	benzaldehyde	50.37	106	2.72
25	2-methyl-2-pentenal	53.82	98	trace
26	2-methylbenzaldehyde	56.28	120	0.83
27	4-methylbenzaldehyde	58.05	120	0.47
28	1-methoxy-4-methylbenzene	66.30	122	5.93
29	1-methoxy-3-methylbenzene	66.58	122	2.41
30	2-isopropylbenzaldehyde	67.06	148	0.75
31	4-phenylbutanone	69.79	148	trace
32	2,4-dimethylanisole	70.13	136	trace
33	4-hexenoic acid	74.90	114	trace
34	3-hexenoic acid	75.30	114	1.22
35	3-phenyl-2-propenal	79.18	132	trace

As seen from Table 6.5.1, in the conditions of flash pyrolysis at 600° C, the level of water is not among the largest in the pyrogram. This indicates that water is not a good leaving molecule as compared to other groups such as hydrohalogenated acids that are eliminated, for example, from poly(vinyl chloride) or poly(vinyl fluoride). The main pyrolysis products are acetaldehyde, several unsaturated aldehydes (2-butenal, 2-methyl-2-propenal, (E,E)-2,4-hexadienal) and 1-methoxy-4-methylbenzene, all still containing the oxygen atom in the molecule. Very few hydrocarbons are present in the pyrogram. This indicates that in flash pyrolysis the cleavage of the backbone of the polymer takes place more easily than the elimination of water. Some oxidation/reduction reactions also are likely to occur since traces of some acids are present. It is likely that the acetic acid (peak 19) is not generated from the pure poly(vinyl alcohol) but from the traces of poly(vinyl acetate) residual in the material used as a sample.

- Poly(vinyl ethers)

A number of poly(vinyl ethers) are used in practice. Their typical structure can be described by the formula $[-CH_2CH(OR)-]_n$, the more common ones being the polymers with R = methyl, ethyl, propyl, n-butyl, or *tert*-butyl. Polymers with longer radical chains such as octadecyl also are known. Poly(vinyl methyl ether) (PVME), CAS# 9003-09-2, with lower DP is a viscous liquid, while the polymer with higher DP is a stiff rubber. PVME is used as a rubber plasticizer and in adhesives and paints. Poly(vinyl ethyl

ether), CAS# 25104-37-4, is used in pressure-sensitive adhesives and as a plasticizer in cellulose nitrate lacquers. The pyrogram of a sample of poly(vinyl methyl ether) (viscous liquid) performed at 600° C in He and with the separation done on a Carbowax column (similar to other examples, e.g. polyethylene) is shown in Figure 6.5.3. The peak identification for the chromatogram displayed in Figure 6.5.3 was done using MS spectral library searches and the results are given in Table 6.5.2.

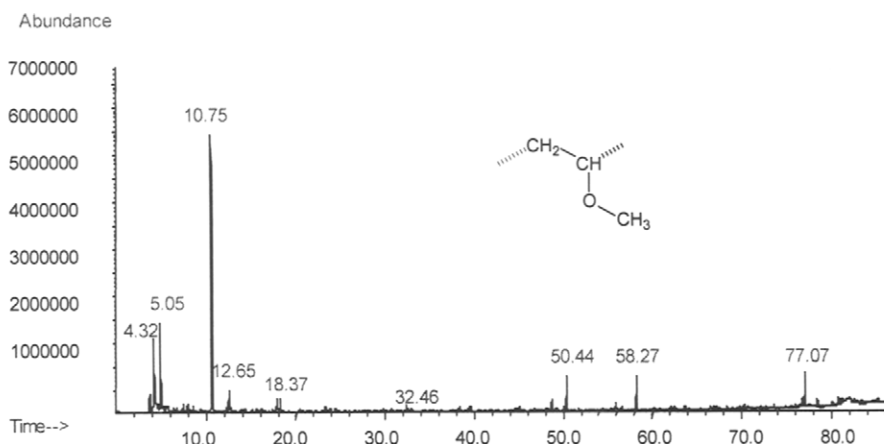


FIGURE 6.5.3. Result for a Py-GC/MS analysis of poly(vinyl methyl ether). Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

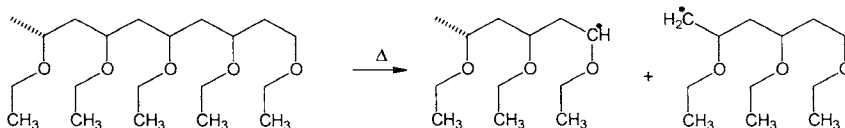
TABLE 6.5.2. Compounds identified in the pyrogram of poly(vinyl methyl ether) as shown in Figure 6.5.3.

Peak	Compound	Ret. Time	MW	Area
1	methane	4.32	16	15.55
2	formaldehyde	5.05	30	14.10
3	acetaldehyde	5.87	44	3.03
4	4-methoxy-1-butene	7.55	88	1.16
5	acetone	8.07	58	1.29
6	methanol	10.76	32	42.80
7	benzene	12.65	78	2.65
8	toluene	17.95	92	2.00
9	water	18.37	18	2.03
10	styrene	32.46	104	0.84
11	methoxybenzene	38.39	108	0.48
12	2,4-dimethoxypentane ?	48.75	132	0.98
13	benzaldehyde	50.44	106	4.08
14	1,4-dihydronaphthalene	55.92	130	1.44
15	1-phenylethanone	58.27	120	3.95
16	phenol	77.07	94	3.61

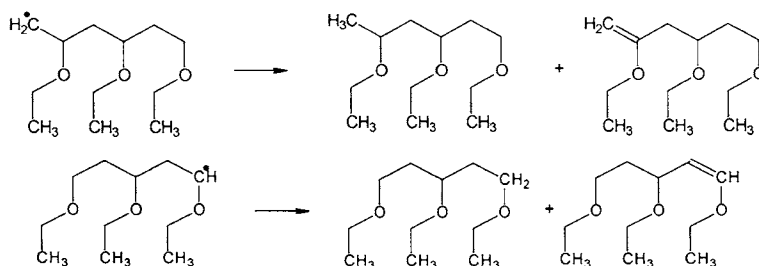
Differently from poly(vinyl alcohol), which does not appear to lose easily the water molecule from the monomer unit, methanol is more easily eliminated from poly(vinyl methyl ether). Some hydrogen migration also takes place in this pyrolysis, methane and some aromatic hydrocarbons being produced.

Pyrolysis of poly(vinyl ethyl ether) with the formula $[-CH_2CH(OC_2H_5)-]_n$ gives similar results to those for the methyl ether. Two pyrograms for poly(vinyl ethyl ether) were shown in Figures 3.1.6 and 3.1.7, and the identification of their peaks was given in Tables 3.1.4 and 3.1.5, respectively (see Section 3.1). The similarity in the pyrolysis results of the poly -methyl and -ethyl vinyl ethers can be noticed by comparing Table 6.5.2 with Tables 3.1.4 and 3.1.5. Methanol is the main pyrolysis product from poly(vinyl methyl ether), and ethanol is the one from poly(vinyl ethyl ether). Formation of aldehydes corresponding to the side chain group is also common, and high yield of formaldehyde is generated from the methyl ether, and acetaldehyde from the ethyl ether. Another compound formed in considerable amount in the pyrolysates of poly(vinyl aliphatic ether) is the saturated hydrocarbon corresponding to the side chain group, like methane from the methyl ether and ethane from the ethyl ether.

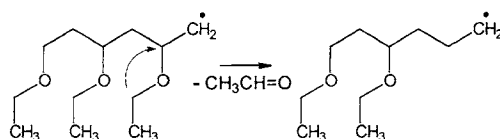
The reactions taking place during the pyrolysis can be rather complex and may occur with both C-C bond cleavage in the polymer backbone or with C-O bond cleavage at the side chain. Depending on the amount of sample used in the pyrolysis and indirectly on the temperatures to which the polymer was exposed, some variability in the peak intensities is noticed when the pyrolysate from a small sample is compared to that for a larger sample. In various conditions, the polymeric chain can be cleaved by random scission reactions, similar to those for polyethylene or polypropylene, as shown below:



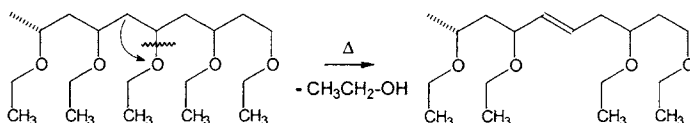
The radicals formed will undergo typical reaction of propagation and termination. Examples of a termination reaction for three units fragment radicals are indicated schematically below:



The radicals formed in this reaction also can eliminate small molecules, as shown for the formation of acetaldehyde:

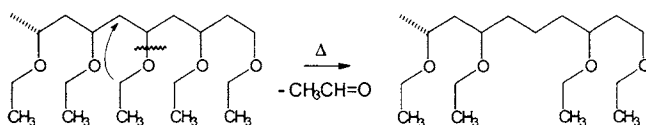


The side chain reactions may play an important role in the thermal decomposition of poly(vinyl ethers). The elimination of an alcohol molecule from the side chain is indicated below:

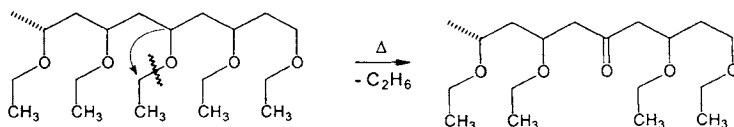


Further cleavage of the chain with double bonds formed after the alcohol elimination explains the formation of some aromatic compounds such as benzene, toluene, styrene, benzaldehyde, etc. Two other common small molecules in the pyrolysate are phenol and the corresponding acid of the side chain substituent.

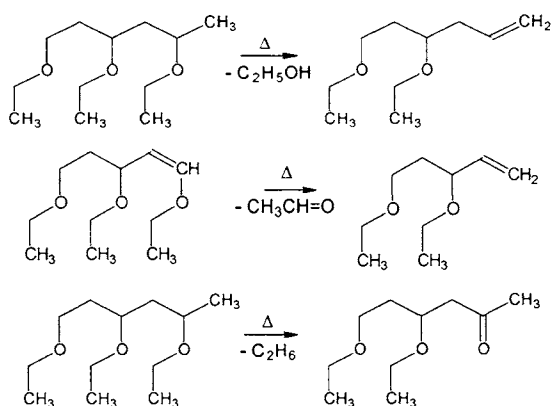
The same bond as in the case of alcohol elimination can break with the formation of acetaldehyde, this time with the migration of a hydrogen from the side chain to the backbone of the polymer:



A considerable proportion of hydrocarbon also is formed in these pyrolysis reactions. The formation of the hydrocarbon is probably the result of the breaking of the O-C bond and migration of a hydrogen from the polymeric backbone in a reaction as follows:



The resulting fragment molecules from the previous reactions may suffer further decomposition generating the same small molecules as the polymer:



One more example of a pyrogram for a vinyl ether is given for poly(vinyl isobutyl ether), CAS# 9003-44-5. The Py-GC/MS experiment was performed in similar conditions as for the other examples previously discussed (see Table 4.2.2). The polymer has the idealized formula $\{-\text{CH}_2\text{CH}[\text{OCH}_2\text{CH}(\text{CH}_3)_2]\}_n$. The pyrogram is given in Figure 6.5.4 and the peak identification is given in Table 6.5.3.

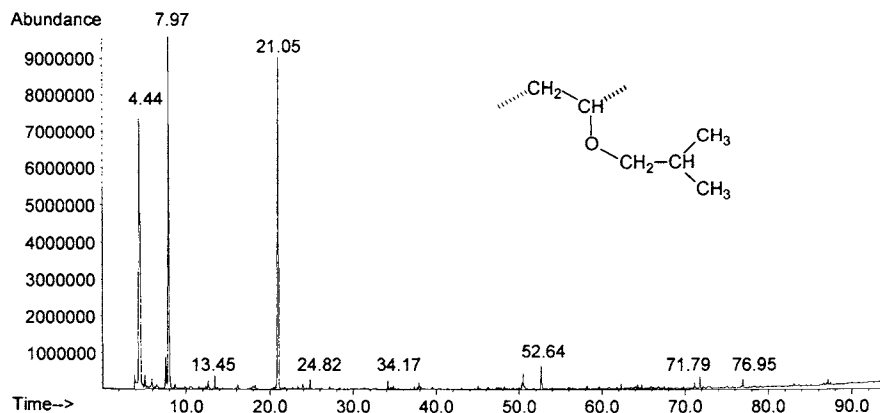


FIGURE 6.5.4. Result for a Py-GC/MS analysis of poly(vinyl isobutyl ether). Pyrolysis done on 0.4 mg material at 600°C in He, with the separation on a Carbowax type column.

TABLE 6.5.3. Compounds identified in the pyrogram of poly(vinyl isobutyl ether) as shown in Figure 6.5.4.

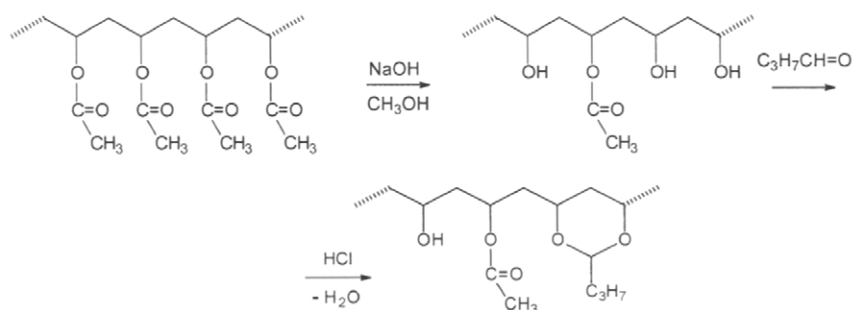
Peak	Compound	Ret. Time	MW	Area %
1	2-methylpropane	4.44	58	23.21
2	2-methyl-1-propene	4.56	56	8.82
3	formaldehyde	5.05	30	0.85
4	acetaldehyde	5.92	44	0.81
5	1-(ethenyloxy)-2-methylpropane (monomer)	7.59	100	2.08
6	2-methylpropanal	7.98	72	29.89
7	benzene + 1-methyl-1-(2-methylpropoxy)-2-propene	12.66	78, 128	0.61
8	1,1-dimethoxy-2-methylpropane ?	13.45	118	0.65
9	acetic acid 2-methylpropyl ester	16.16	116	trace
10	toluene	17.95	92	trace
11	2-methyl-1-propanol	21.05	74	28.88
12	1,2-bis(2-methylpropoxy)ethane	24.82	174	0.52
13	butanoic acid 1,1-dimethylethyl ester	34.17	144	0.46
14	1,2-bis(2-methylpropoxy)-1-methylpropane	50.47	202	0.63
15	2-methylpropanoic acid	52.64	88	1.36
16	1,2,3-tris(2-methylpropoxy)prop-1-ene	71.79	258	0.62
17	phenol	76.95	94	0.60

Similar to the other two examples, the alcohol, the corresponding aldehyde, and the hydrocarbon are found in large proportions in the pyrolysate. Also, phenol and the corresponding acid of the side chain substituent are present, similar to the examples of methyl and ethyl ethers.

Other studies on thermal behavior of vinyl ethers reported in literature include that for poly(trifluorovinyl phenyl ether) [12], poly(divinyl ether), etc.

- Poly(vinyl acetals)

The -O-R group attached to the carbon chain backbone of a polymer is also present in acetals. These polymers can be obtained, for example, from poly(vinyl alcohol) and an aldehyde in the presence of a strong acid. Typically the reaction starts with poly(vinyl acetate), which is saponified in methanol with NaOH to generate the PVA, followed by the acetal formation. This sequence of reactions is shown below for the formation of poly(vinyl butyral):



As suggested in the sequence of reactions shown above, the saponification of the poly(vinyl acetate) usually is not complete, and the formation of the acetal from the alcohol groups also is incomplete. For this reason, the final polymer formed in the reaction has the formula $[(C_8H_{14}O_2)_x(C_2H_4O)_y(C_4H_8O_2)_z]_n$ and is a copolymer named poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate). This material is used as a laminate in safety glass for automotive use, in bulletproof and other glass products. Other uses are as ceramic binders, surface coatings for wood, structural adhesives (combined with other resins) in printed circuits, inks and dyes, paints; solder masks and hot melt adhesives. Also, it is used to improve water and stain resistance of textiles.

Since it is difficult to have poly(vinyl butyral) as homopolymer, a pyrogram for the copolymer with CAS# 27360-07-2, which is poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate), is shown in Figure 6.5.5. The pyrolysis was done in similar conditions to those used for other polymers previously discussed (see Table 4.2.2). The peak identification for the chromatogram displayed in Figure 6.5.5 was done using MS spectral library searches only and the results are given in Table 6.5.4.

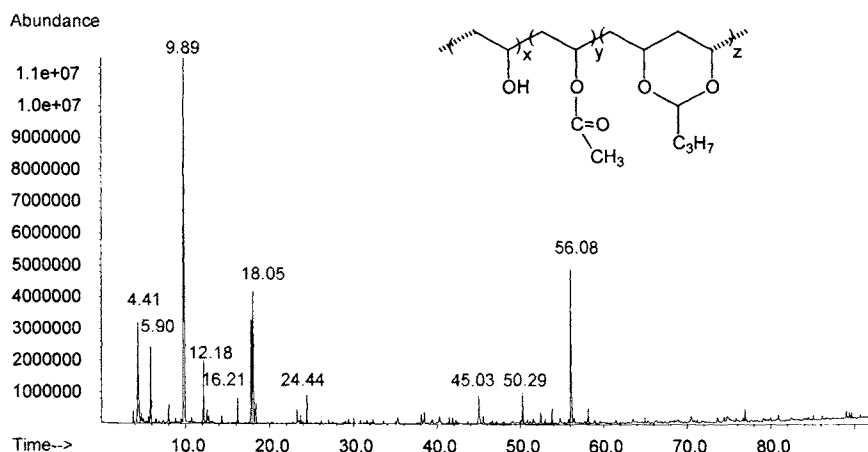


FIGURE 6.5.5. Result for a Py-GC/MS analysis of poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate) $M_w = 50,000\text{--}80,000$. Pyrolysis done on 0.4 mg material at 600°C in He, with the separation on a Carbowax type column.

It is rather difficult to assess which peaks are generated exclusively from the poly(vinyl butyral) component and which are generated from the other components. It is likely that the acetic acid is formed from the acetate. Other components are consistent with the decomposition of the acetal that behaves somehow similar to an ether. However, the formation of the hydrocarbon (butane) is significantly reduced, as well as that of the alcohol (butanol). On the other hand, the formation of the corresponding aldehyde (butanal) is significant.

TABLE 6.5.4. Compounds identified in the pyrogram of poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate) as shown in Figure 6.5.5.

Peak	Compound	Ret. Time	MW	Area %
1	carbon dioxide	4.41	44	2.65
2	propane	4.55	44	2.44
3	propene	4.60	42	2.44
4	butane	4.66	56	2.44
5	1,3-butadiene	4.77	54	trace
6	acetaldehyde	5.90	44	6.46
7	propanone	8.03	58	2.48
8	propenal	8.81	56	trace
9	butanal	9.89	72	34.71
10	2,5-dihydrofuran	12.18	70	4.05
11	benzene	12.60	78	1.30
12	3-buten-2-one	12.79	70	trace
13	2-pentanone	14.31	86	trace
14	3-penten-2-one	16.21	84	1.45
15	2-butenal	17.84	70	6.72
16	2-methyl-2-propenal	18.07	70	9.02
17	water	18.36	18	2.09
18	3-methyl-3-buten-2-one	23.29	84	1.44
19	5-hexenal	23.60	98	trace
20	1-butanol	24.44	74	1.85
21	styrene	32.33	104	trace
22	acetic acid	45.03	60	3.02
23	2,2-dimethyl-4-cyclopentene-1-one	45.49	110	trace
24	benzaldehyde	50.29	106	2.28
25	butanoic acid	56.08	88	11.82
26	4-methylbenzaldehyde	58.05	120	1.34

- Poly(vinyl ketones)

Poly(vinyl ketones) such as poly(ethylene-*alt*-carbon monoxide) CAS# 111190-67-1, poly(methyl vinyl ketone) CAS# 25038-87-3, and poly(methyl isopropenyl ketone) CAS# 25988-32-3, also have practical applications. For example, poly(ethylene-*alt*-carbon monoxide) is used in photodegradable plastics and in various copolymers. Several studies were reported regarding the thermal stability of these polymers. It has been shown that poly(ethylene-*alt*-carbon monoxide) decomposes upon heating with chain scission generating small molecular weight alkenes and ketones. Some literature reports discussing the thermal decomposition of poly(vinyl ketones) are summarized in Table 6.5.5 [13].

TABLE 6.5.5. Summary regarding literature information on thermal decomposition of some poly(vinyl ketones).

Polymer	Temp. °C	Results	Ref.
poly(ethylene-alt-carbon monoxide)	500	CO, H ₂ O, ethene, series of ketones with general structure R-[-CO-CH ₂ -CH ₂ -] _n -CO-R' where R, R' = -CH ₃ , -CH ₂ -CH ₃ or -CH=CH ₂	14
poly(methyl isopropenyl ketone)	270-360	H ₂ O	15
poly(methyl isopropenyl ketone)	ambient to 500	methyl isopropenyl ketone (50%), modified chain fragments, H ₂ O, small amounts of CH ₄ and CO	16
poly(methyl isopropenyl ketone)	150-190	monomer under 313 nm radiation	17
poly(methyl vinyl ketone)	270-360	H ₂ O, 3-methyl-2-cyclohexene-1-one and other six-membered ring ketones	18
poly(methyl vinyl ketone)	ambient to 500	H ₂ O, modified chain fragments, small amounts of CH ₄ and CO	16

A pyrogram for poly(vinyl methyl ketone) $\{-CH_2CH[C(O)-CH_3]\}_n$, $M_w = 500,000$ is shown in Figure 6.5.6. The pyrolysis was done in similar conditions to those used for other polymers previously discussed, at 600° C in He at a heating rate of 20° C/ms, starting with 0.4 mg sample and with the separation on a Carbowax column (see Table 4.2.2). The peak identification for the chromatogram displayed in Figure 6.5.6 was done using MS spectral library searches and the results are given in Table 6.5.6.

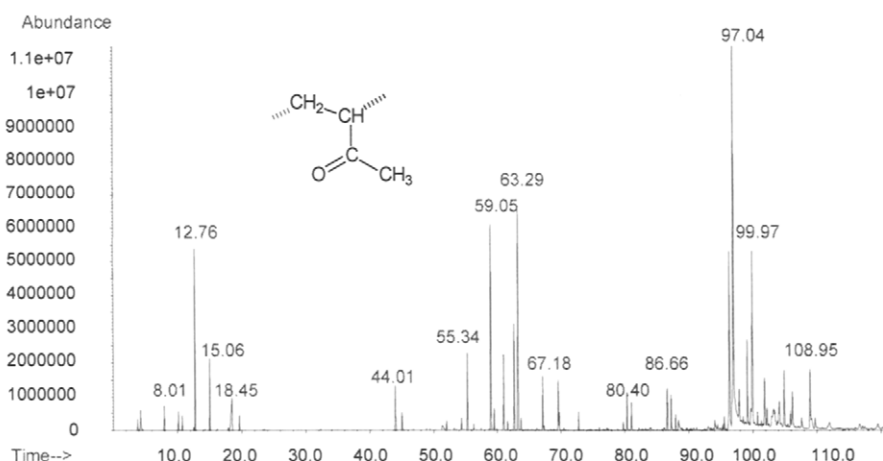
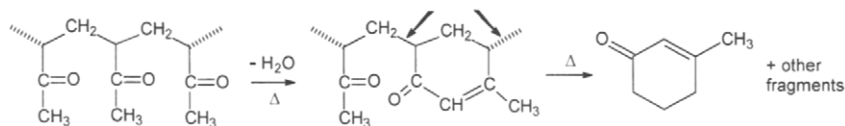


FIGURE 6.5.6. Result for a Py-GC/MS analysis of poly(vinyl methyl ketone), $M_w = 500,000$. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 6.5.6. Compounds identified in the pyrogram of poly(vinyl methyl ketone) as shown in Figure 6.5.6.

Peak	Compound	Ret. Time	MW	Area %
1	carbon dioxide	4.31	44	0.98
2	acetone	8.01	58	0.67
3	ethyl acetate	10.17	88	0.36
4	2-butanone	10.77	72	0.32
5	3-buten-2-one (monomer)	12.77	70	5.02
6	3-methyl-3-buten-2-one	15.06	84	1.76
7	water	18.45	18	2.19
8	3-methylene-2-pentanone	19.65	98	0.34
9	3-methyl-3-cyclohexen-1-one	44.01	110	1.58
10	acetic acid	45.07	60	0.56
11	3-ethenylcyclopentene	51.40	94	trace
12	4,5-dimethyl-2-cyclohexen-1-one	52.05	124	trace
13	3,5-dimethyl-2-cyclohexen-1-one	54.40	124	trace
14	3-methyl-2-cyclohexen-1-one	55.34	110	2.37
15	2,6-heptandione	59.06	128	7.74
16	2,6-octandione	59.55	142	0.58
17	3-vinylcyclohex-2-en-1-one	61.06	122	2.29
18	5-vinylcyclohex-2-en-1-one	62.70	122	3.27
19	3-methyleneheptane-2,6-dione ?	63.30	140	7.36
20	3-prop-2-enylhex-5-ene-2,4-dione	67.18	152	1.64
21	?-ethenylmethoxybenzene	69.59	134	2.01
22	4-phenyl-2-butanone	69.75	148	trace
23	3-methyl-4-phenyl-3-buten-2-one	72.79	160	0.49
24	2,5-dimethylphenol	80.40	122	1.08
25	3-methylphenol	81.08	108	0.82
26	2,4,5-trimethylphenol	86.66	136	1.14
27	3,4-dimethylphenol	87.28	122	1.11
28	1,4-dimethyl-1,2,3,4-tetrahydronaphthalene	87.97	160	0.54
29	3-methyl-5-(3-oxobutyl)cyclohex-2-en-1-one	96.42	180	7.76
30	5-acetyl-3-methylenenonane-2,8-dione ?	97.04	210	22.00
31	unknown [43(100), 179(39), 204(22), 137(15), 119(14)]	97.90		2.88
32	5-(1-ethylbut-3-enyl)-3-methylcyclohex-2-en-1-one ?	99.17	192	3.46
33	unknown [134(100), 122(52), 121(45), 107(41), 91(25), ...192(6)]	99.97	192	7.83
34	3,4-dihydro-5,8-dimethyl-1(2H)-naphthalenone	101.88	174	2.64
35	unknown [134(100), 135(41), 91(23), 121(14), 43(14)]	104.93		2.23
36	unknown [43(100), 97(74), 125(62), 192(40), 85(42)]	106.17		1.66
37	unknown [43(100), 149(56), 150(48), 121(19), 125(17), 192(11)]	108.95		3.30

As seen from Figure 6.5.6, the pyrogram of poly(vinyl methyl ketone) shows a significant number of components. The polymer starts decomposing at about 200° C, undergoing initially an aldol condensation [19–21]. The formation during pyrolysis of 3-methyl-2-cyclohexene-1-one (2.4%) from poly(methyl vinyl ketone) in the aldol condensation is shown below:



This reaction is not the only one that occurs in the pyrolysis. Some monomer (5%) is formed, indicating that some chain scission takes place prior to aldol condensation. The

formation of the dimer or 3-methyleneheptane-2,6-dione (7.4%) and that of trimer or 5-acetyl-3-methylenonane-2,8-dione (22.0%) is very likely to happen, although the peak identification for these two compounds is only tentative. The mass spectrum for the peak eluting at 63.30 min. is shown in Figure 6.5.7 and that of peak eluting at 97.04 min. is shown in Figure 6.5.8.

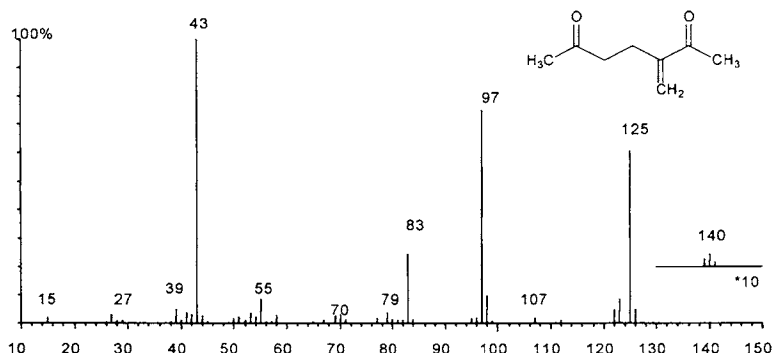


FIGURE 6.5.7. Mass spectrum tentatively identified as 3-methyleneheptane-2,6-dione (MW = 140).

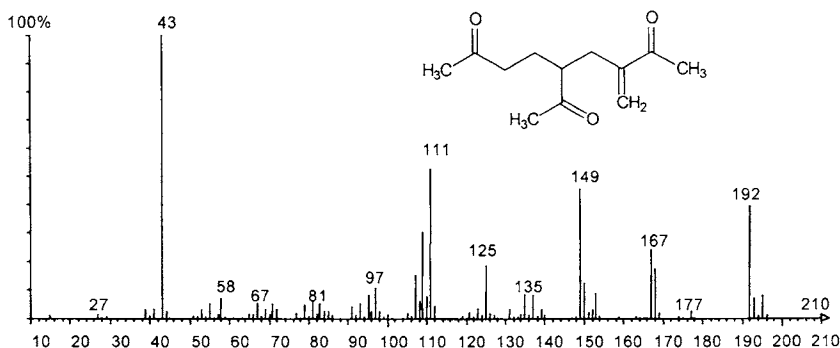


FIGURE 6.5.8. Mass spectrum tentatively identified as 5-acetyl-3-methylenonane-2,8-dione (MW = 210).

Formation of some aromatic compounds show that further eliminations after the aldol condensation may take place with formation of phenol derivatives. Also, larger fragments seen in the last part of the pyrogram show that the backbone of the polymer is not cleaved only in the manner involved in the formation of 3-methyl-2-cyclohexene-1-one. Similar pyrolysis occurs for poly(methyl isopropenyl ketone), which starts decomposing at about 250° C (a change in color starts at 170° C), also undergoing an aldol condensation.

Another example of a pyrogram of a poly(vinyl ketone) is that of poly(vinyl phenyl ketone), CAS# 768-03-6, with the structure $\{-\text{CH}_2\text{CH}[\text{C}(\text{O})-\text{C}_6\text{H}_5]-\}_n$. This pyrogram is shown in Figure 6.5.9. The pyrolysis was done similarly to that of other examples, at

600° C in He at a heating rate of 20° C/ms starting with 0.4 mg sample and with separation on a Carbowax column (see Table 4.2.2). Identification of peaks in the pyrogram was done using MS spectral library searches only and is given in Table 6.5.7.

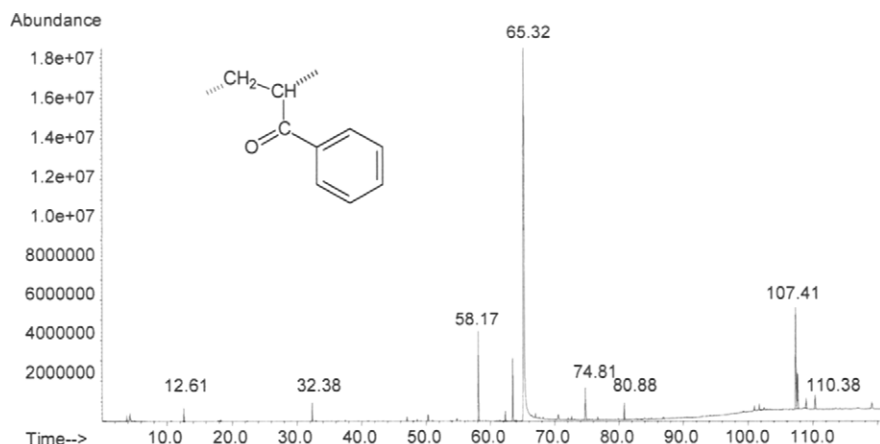


FIGURE 6.5.9. Result for a Py-GC/MS analysis of poly(vinyl phenyl ketone). Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 6.5.7. Compounds identified in the pyrogram of poly(vinyl phenyl ketone) as shown in Figure 6.5.9.

Peak	Compound	Ret. Time	MW	Area %
1	ethene	4.34	28	1.23
2	formaldehyde	5.04	30	trace
3	benzene	12.61	78	0.88
4	toluene	17.95	92	trace
5	water	18.34	18	trace
6	styrene	32.38	104	1.23
7	α -methylstyrene	37.47	118	trace
8	1-methyl-1-propenylbenzene	47.03	132	trace
9	benzaldehyde	50.31	106	trace
10	2-methylbenzofuran	54.48	132	trace
11	1-phenylethanone	58.17	120	6.57
12	1-phenylpropanone	62.35	134	0.71
13	2-methyl-1-phenyl-2-propen-1-one	63.52	146	4.61
14	1-phenyl-2-propen-1-one (monomer)	65.32	132	64.37
15	1-benzoyl-1-propene	70.58	146	trace
16	4-methyl-1-naphthalenol	72.35	158	trace
17	cyclobutyl phenyl ketone	74.81	160	2.75
18	1,1'-biphenyl	76.71	154	trace
19	unknown [175(100), 105(63), 77(41), 176(18), 51(9)]	80.88		1.33
20	1,2-diphenylethanone	107.41	196	10.11
21	1,4-diphenyl-2-buten-1,4-dione	107.69	236	3.39
22	1,2-diphenyl-2-propen-1-one	108.97	208	1.29
23	1,3-diphenyl-2-buten-1-one	110.38	222	1.53
24	2-benzyl-3,4-dihydro-1(2H)-naphthalenone ?	119.08	236	trace

The pyrolysis of poly(vinyl phenyl ketone) does not follow the same mechanism as that of poly(vinyl methyl ketone), since an aldol condensation is not possible when the side chain substituent at the keto group is phenyl. This can be seen from the identification for the peaks in the chromatogram displayed in Figure 6.5.9.

The main product of the pyrolysis of poly(vinyl phenyl ketone) is the monomer, 1-phenyl-2-propen-1-one. This would be the indication that the pyrolysis of this polymer takes place by an unzipping free radical reaction.

- Poly(vinyl esters)

The most common polymer of a vinyl ester is poly(vinyl acetate), CAS# 9003-20-7, with the formula $[-CH_2CH(OC(O)CH_3)-]_n$. Other vinyl esters also are known, such as poly(vinyl butyrate), poly(vinyl benzoate) CAS# 24991-32-0, and poly(vinyltrifluoroacetate), CAS# 25748-85-0. Poly(vinyl acetate) is typically obtained from the monomer with radical initiators, either by emulsion or suspension polymerization. The polymer is used in water-based emulsion paints, adhesives [22], gum base for chewing gum, etc. Also, poly(vinyl acetate) is used as a precursor for the preparation of other polymers such as poly(vinyl alcohol) or poly(vinyl acetals). Thermal decomposition of poly(vinyl acetate) starts at a relatively low temperature, around 200° C, some of the reports regarding its thermal decomposition being given in Table 6.5.8 [13]. The same table includes references for poly(vinyl butyrate) and poly(vinyl cinnamate), CAS# 9050-06-0.

TABLE 6.5.8. Summary regarding literature information on thermal decomposition of several poly(vinyl esters).

Polymer	Temp. °C	Results	Ref.
poly(vinyl acetate)	213–235	quantitative yields of acetic acid	23
poly(vinyl acetate)	300	small amounts of aromatics including benzene	23
poly(vinyl acetate)	500 flash in He	benzene, toluene, ethylbenzene, indane, indene, propylbenzene, methylindane, divinylbenzene, naphthalene, methylnaphthalene, dimethylnaphthalene, biphenyl, acenaphthene	24
poly(vinyl acetate)	280–350	acetic acid, benzene, naphthalene, toluene, styrene, ethylbenzene, propenylbenzene, propylbenzene, methylnaphthalene, ethylnaphthalene, propenylnaphthalene, propylnaphthalene, anthracene, methylantracene, ethylantracene, propylantracene	25
poly(vinyl acetate) and ZnBr ₂	ambient to 500	acetic acid produced as low as 100° C	26
poly(vinyl butyrate)	300–325	butyric acid	27
poly(vinyl cinnamate)	600 (flash)	carbon dioxide 0.83, benzene 1.31, toluene 1.59, styrene 0.78, benzaldehyde 0.45, naphthalene 0.33, biphenyl 0.35, cinnamaldehyde 0.21, cinnamic acid isopropyl ester 1.92, 1,1'-(1,2-ethylenediyl)bis-benzene 0.72, 3-phenylpropanoic acid 1.66, 3-phenyl-2-propenoic acid (cinnamic acid) 87.39	28

An example of a pyrogram for a poly(vinyl acetate) sample ($M_w = 200,000$) is shown in Figure 6.5.10. The pyrolysis was done at 600° C in He with separation on a Carbowax column and MS detection, similarly to other polymers previously discussed in this book (see Table 4.2.2). The peak identification for the chromatogram shown in Figure 6.5.10 was done using MS spectral library searches and is given in Table 6.5.9.

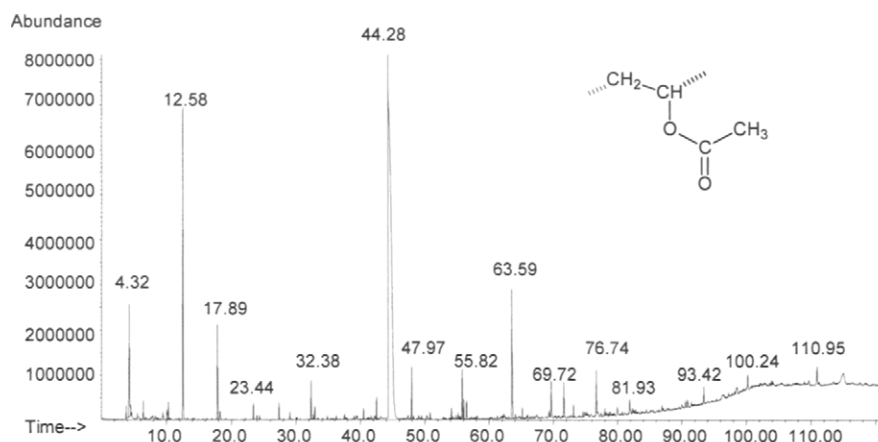


FIGURE 6.5.10. Result for a Py-GC/MS analysis of poly(vinyl acetate). Pyrolysis done on 0.4 mg material with $M_w = 280,000$, at 600°C in He, with the separation on a Carbowax type column.

TABLE 6.5.9. Compounds identified in the pyrogram of poly(vinyl acetate) shown in Figure 6.5.10.

Peak	Compound	Ret. Time	MW	Area %
1	carbon dioxide	4.32	44	2.89
2	ethenone (ketene) ?	4.55	42	0.27
3	butadiene	4.70	54	trace
4	cyclopentene	5.59	68	trace
5	1,3-cyclopentadiene	6.47	66	0.46
6	1,3-butandione	10.12	86	0.41
7	acetic acid vinyl ester (monomer)	10.36	86	0.52
8	benzene	12.58	78	8.91
9	toluene	17.89	92	3.07
10	ethylbenzene	23.44	106	0.50
11	1,3-dimethylbenzene	23.95	106	trace
12	1,2-dimethylbenzene	24.40	106	trace
13	1,4-dimethylbenzene	27.41	106	0.51
14	propylbenzene	29.07	120	trace
15	styrene	32.38	104	1.12
16	1-ethyl-2-methylbenzene	32.75	120	trace
17	1-ethenyl-4-methylbenzene	32.96	118	0.35
18	butylbenzene	34.26	134	trace
19	1-propenylbenzene	37.55	118	trace
20	indane	40.50	118	0.33
21	2-butenylbenzene	41.66	132	trace
22	2-propenylbenzene	42.50	118	0.66
23	acetic acid	44.28	60	63.76
24	1H-indene	47.97	116	1.62
25	1,2,3,4-tetrahydronaphthalene	50.81	132	trace
26	2-methylindene	54.15	130	0.38
27	1-methylindene	55.17	130	trace
28	1,4-dihydronaphthalene	55.82	130	1.69

TABLE 6.5.9 (continued). Compounds identified in the pyrogram of poly(vinyl acetate) shown in Figure 6.5.10.

Peak	Compound	Ret. Time	MW	Area %
29	acetic acid phenyl ester	56.06	136	0.58
30	1-methylene-2-propenylbenzene	56.51	130	0.55
31	naphthalene	63.59	128	4.27
32	octadecane	65.19	254	0.36
33	benzocycloheptatriene	69.35	142	trace
34	1-methylnaphthalene	69.72	142	1.25
35	2-methylnaphthalene	71.68	142	1.14
36	2-methyl-1,1'-biphenyl	73.16	168	0.39
37	1-ethylnaphthalene	74.60	156	trace
38	1,1'-biphenyl	76.74	154	1.30
39	diphenylmethane	78.02	168	trace
40	2-ethylnaphthalene	81.93	154	0.63
41	9H-fluorene	93.42	166	0.56
42	1,1'-(1,2-ethandiyl)bis-benzene	100.24	180	0.64
43	phenanthrene	110.95	178	0.87

The pyrolysis of vinyl esters typically occurs with the elimination of the acid, followed by the breaking of the carbon chain containing double bonds and the formation of unsaturated and aromatic hydrocarbons. Depending on the pyrolysis temperature, the acid may undergo some decarboxylation, and CO₂ is frequently seen in the pyrograms. For the experimental conditions used in the pyrolysis of poly(vinyl acetate) described in Figure 6.5.8, aromatic hydrocarbons only up to fluorene are noticed. Possibly, higher polycyclic aromatic hydrocarbons (PAHs) also are formed in these reactions, but they are not detected in the conditions typically applied for on-line analytical pyrolysis. This is caused by the very low levels of PAHs in pyrolysate, and because the elution of PAHs from the chromatographic column is a problem if the upper temperature used for the GC separation is not high enough.

- Other substituted polyvinyls

Many other vinyl polymers are known and have practical applications. For example, poly(vinylpyrrolidone) or PVP, CAS# 25249-54-1, is used as a binder for printing inks, foam stabilizer, gelling agent, and water soluble thickening agent for hairsprays and cosmetics. It is used in adhesives, detergents, and paints as a protective colloid or dispersion agent, in making controlled release pharmaceutical devices, etc. Poly(2-vinylpyridine), CAS# 9003-47-8, is used as an ion exchanger in quaternized form, as a flocculent, an antimicrobial resin, adsorption material for metal ions and phenols from wastewater, etc. The carbazole polymers such as poly(9-vinylcarbazole), CAS# 25067-59-8, or its copolymers with alkyl methacrylates are used as photoconducting polymers [29] in the reproduction graphics industry, etc.

Some results regarding thermal decomposition of various vinyl polymers from this group are summarized in Table 6.5.10. The polymer list includes poly(*tert*-butyl-*N*-vinyl carbamate), poly(*N*-vinylcarbazole), two halogenated poly(*N*-vinylcarbazoles), two poly(vinylpyridines), and poly(vinyltrimethyl-silane).

TABLE 6.5.10. Summary regarding literature on thermal decomposition of several substituted vinyl polymers.

Polymer	Temp. °C	Results	Ref.
poly(<i>tert</i> -butyl-N-vinyl carbamate)	185–220	equal amounts of CO ₂ and isobutylene, in yields ranging from 43 to 60%	30
poly(N-vinylcarbazole)	230–410	below 350° C, monomer; above 350° C, monomer and low-molecular weight oligomers	31
poly(N-vinylcarbazole)	300–500	monomer (49% of total volatiles at 300° C, 39% at 500° C) ethane, ethene, propene, n-butane, isobutene, <i>cis</i> and <i>trans</i> -but-2-ene, 1,3-butadiene, 2-methylbutadiene, trace amounts of C ₅ and C ₆ hydrocarbons	32
poly(N-vinylcarbazole) M _w = 1,100,000	600 (flash)	9-ethenylcarbazole (monomer) 49.60%, carbazole 50%, 2-propanone 0.23%, styrene 0.06%, 9-ethyl-9H-carbazole 0.12%, and traces of benzene, 5,5-dimethyl-1,3-cyclopentadiene, 2-methyl-2propenenitrile, 1,3,5-heptatriene, 3-methyl-1,3,5-hexatriene, toluene, as well as some char	28
poly(3,6-dichloro-N-vinylcarbazole)	300–500	monomer (83% of total volatiles at 300° C, 67% at 500° C), ethane, ethene, propene, n-butane, isobutene, <i>cis</i> and <i>trans</i> but-2-ene, 1,3-butadiene, 2-methylbutadiene, trace amounts of C ₅ and C ₆ hydrocarbons	32
poly(3,6-dibromo-N-vinylcarbazole)	300–500	monomer (48% of total volatiles at 350° C, 40% at 500° C), ethane, ethene, propene, n-butane, isobutene, <i>cis</i> and <i>trans</i> but-2-ene, 1,3-butadiene, 2-methylbutadiene, trace amounts of C ₅ and C ₆ hydrocarbons	32
poly(2-vinylpyridine)	396	monomer, no char	33
poly(4-vinylpyridine)	ambient to 500	monomer, traces of pyridine and 4-methylpyridine	34
poly(vinyltrimethylsilane)	300–600 in argon	tetramethylsilane, trimethylvinylsilane, 2-trimethylsilylpropene, 1,3-di-(trimethylsilyl)propane, 1,3-di-(trimethylsilyl)propene, 2,4-di-(trimethylsilyl)butene 1,2,4,6-tetra(trimethylsilyl)hexene	35
poly(allylamine)	700	methylamine, allylamine, isobutylnitrile, methylpyridine(s), dimethylpyridine(s), dimethylquinoline, trimethylquinoline	36
poly(di- <i>iso</i> -butyl itaconate)	ambient to 500	depolymerization the main process	37
poly(ditetrahydrofurfuryl itaconate)	600	depolymerization is the main process; two degradation mechanisms can be assumed, one being end chain β -scission and the other being random scission	38
poly(di- <i>n</i> -butyl itaconate)	ambient to 500	deesterification the main process	37
poly(di- <i>sec</i> -butyl itaconate)	ambient to 500	deesterification the main process	37

An interesting comparison regarding the effect of different substituents on pyrolysis results for a polymer can be obtained from the Py-GC/MS analysis of a poly(2-vinylpyridine) and that of a poly(4-vinylpyridine) sample. The sample of poly(2-vinylpyridine) has a M_w = 5,000. The pyrolysis was done for both samples from 0.4 mg material, at 600° C in He, at a heating rate of 20° C/ms with 10 s THT, and with the separation on a Carbowax column (see Table 4.2.2). The pyrogram for poly(2-vinylpyridine) is shown in Figure 6.5.11 with the peak identification in Table 6.5.11 (see Figure 6.5.13 for the pyrogram of poly(4-vinylpyridine)).

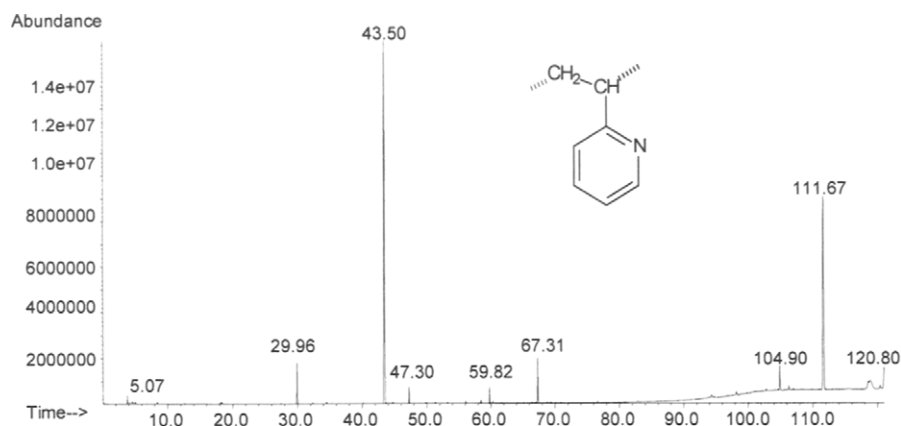


FIGURE 6.5.11. Result for a Py-GC/MS analysis of poly(2-vinylpyridine) $M_w = 5,000$. Pyrolysis done at 600°C in He, with the separation on a Carbowax type column.

TABLE 6.5.11. Compounds identified in the pyrogram of poly(2-vinylpyridine) shown in Figure 6.5.11.

Peak	Compound	Ret. Time	MW	Area%
1	1-pentene	5.07	70	0.14
2	pyridine	27.49	79	trace
3	2-methylpyridine	29.96	93	3.74
4	2-ethenylpyridine (monomer)	43.50	105	55.13
5	2,3-dihydro-1H-indole	47.30	119	1.48
6	2-hexylpyridine	59.82	163	1.47
7	2-(1-methylhex-?-enyl)pyridine	67.31	175	4.14
8	2,2'-(1,3-propandiy)bis-pyridine	104.90	198	2.80
9	2-[3-(2-pyridyl)but-1-enyl]pyridine (dimer)	111.67	210	30.02
10	2-[1-pentyl-3-(2-pyridyl)but-?-enyl]pyridine	120.80	280	1.09

Some of the peak identifications given in Table 6.5.11 are tentative only. For example, the spectrum for 2-[3-(2-pyridyl)but-1-enyl]pyridine is not available in common mass spectral libraries. The tentatively assigned spectrum for this substance is shown in Figure 6.5.12.

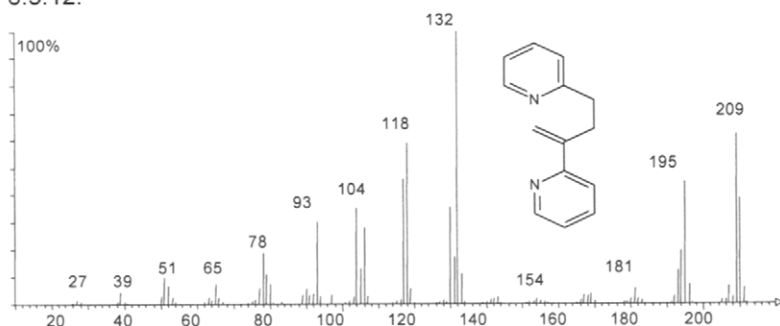


FIGURE 6.5.12. Mass spectrum tentatively assigned to 2-[3-(2-pyridyl)but-1-enyl]pyridine.

The Py-GC/MS experiment for poly(4-vinylpyridine) uses a sample with $M_w = 60,000$. The pyrolysis was done in the same conditions as for poly(2-vinylpyridine). The pyrogram for poly(4-vinylpyridine) is shown in Figure 6.5.13 with the peak identification in Table 6.5.12.

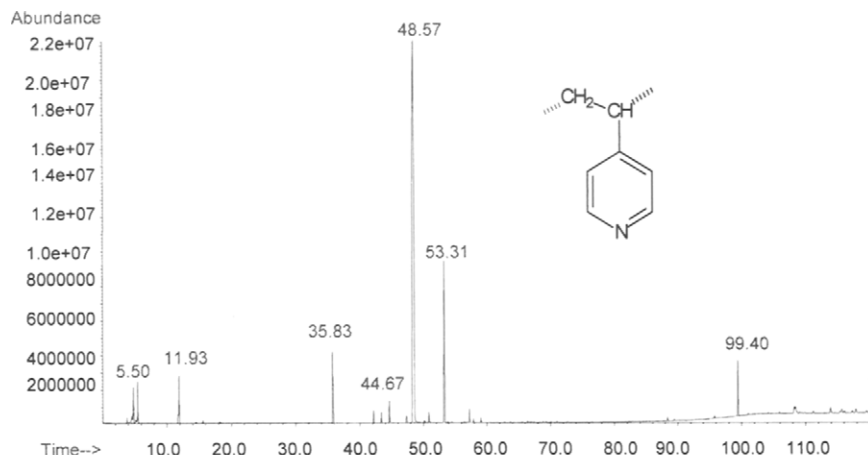


FIGURE 6.5.13. Result for a Py-GC/MS analysis of poly(4-vinylpyridine) $M_w = 60,000$. Pyrolysis done at 600°C in He, with the separation on a Carbowax type column.

TABLE 6.5.12. Compounds identified in the pyrogram of poly(4-vinylpyridine) shown in Figure 6.5.13.

Peak	Compound	Ret. Time	MW	Area %
1	2-methylpentane	4.68	86	0.21
2	3-methylpentane	4.78	86	0.73
3	hexane	4.86	86	1.59
4	methylcyclopentane	5.50	84	1.89
5	2-propanol ?	11.93	60	3.05
6	2-methylpropanenitrile	15.60	69	trace
7	pyridine	27.49	79	trace
8	4-methylpyridine	35.83	93	4.07
9	4-ethylpyridine	42.19	107	0.69
10	2-ethenylpyridine	43.40	105	0.57
11	5-ethenyl-2-methylpyridine	44.68	119	1.18
12	2,3-dihydro-1H-indole	47.33	119	trace
13	4-ethenylpyridine (monomer)	48.57	105	71.27
14	2,3-cyclopentenopyridine	50.89	119	0.74
15	4-isopropenylpyridine	53.31	119	9.89
16	2,2'-azobis-(2-methylpropanenitrile)	57.28	164	0.86
17	?-ethenyl-?-methylpyridine	59.05	119	trace
18	unknown [186(100), 118(88), 117(82), 91(52), 119(30), 171(15)]	99.40		3.25
19	4-[2-(4-pyridyl)ethenyl]pyridine	108.19	182	trace
20	bis-(4-pyridyl)methane	108.40	170	trace
21	4-[3-(4-pyridyl)pent-?-enyl]pyridine	113.86	224	trace

Pyrolysis of poly(4-vinyl pyridine) was demonstrated to be a free radical process. Both poly(vinyl pyridines) generate as a main pyrolysis product the monomer, 2-ethenylpyridine or 4-ethenylpyridine, respectively. In the pyrogram of poly(2-vinyl pyridine), the dimer is also present (30% of the peak area). This peak is not seen in the pyrogram of poly(4-vinyl pyridine), but it is possible that the compound exists and elutes at a longer retention time than the one used in the chromatographic conditions applied for the pyrolysate separation. Other pyrolysate components not shown in Table 6.5.11 or 6.5.13 were reported in literature. Among these are propenylpyridine, isopropylpyridine, isoquinoline, phenylpyridine, 4,4'-dipyridyl, 4-[2-(4-pyridyl)ethyl]pyridine, 4-[2-(4-pyridyl)ethenyl]pyridine, 4-[3-(4-pyridyl)propyl]pyridine, etc. [39]. Similarly to the case of polystyrene, the H-T polymerization is prevalent in poly(vinylpyridine). However, some H-H units can be present in the polymer, and their abundance can be estimated from Py-GC/MS data.

The results for the Py-GC/MS analysis for polymers with a nitrogen atom directly bound to the carbon saturated chain are further exemplified for poly(N-vinyl-pyrrolidone) (cross-linked), CAS# 25249-54-1. Poly(vinylpyrrolidone) (PVP) undergoes a cross-linking process when heated above 150° [40]. The pyrogram for 0.4 mg of a crosslinked polymer is given in Figure 6.5.14. All the conditions for the Py-GC/MS analysis were similar to those for other examples previously discussed in this book (see Table 4.2.2). The peak identification for the pyrogram shown in Figure 6.5.14 is given in Table 6.5.13.

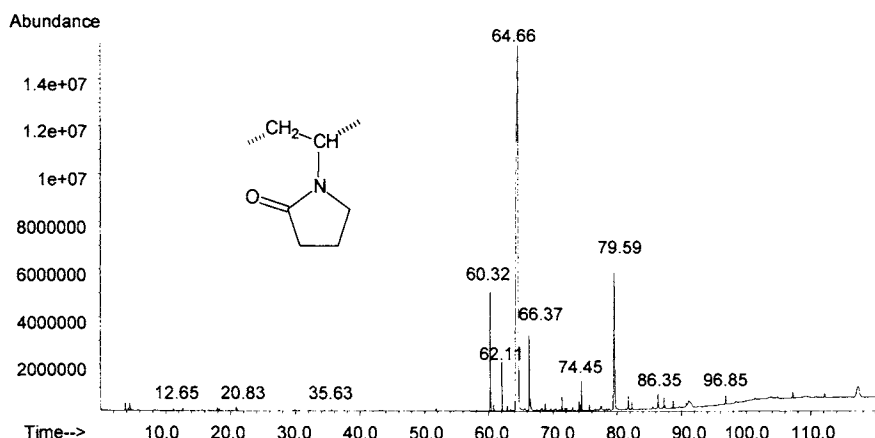


FIGURE 6.5.14. Result for a Py-GC/MS analysis of poly(N-vinyl-2-pyrrolidone) cross-linked. Pyrolysis done at 600° C in He, with the separation on a Carbowax type column.

TABLE 6.5.13. Compounds identified in the pyrogram of poly(*N*-vinyl-2-pyrrolidone) shown in Figure 6.5.14.

Peak	Compound	Ret. Time	MW	Area %
1	1-isocyanatopropane	11.20	85	trace
2	benzene	12.65	78	trace
3	acetonitrile	15.65	41	trace
4	toluene	17.92	92	trace
5	2,3,4,5-tetrahydropyridine	20.83	83	trace
6	2-methylpyridine	29.96	83	trace
7	2-ethyl-6-methylpyridine	35.63	121	trace
8	2,5-dimethylpyridine	37.56	107	trace
9	2-methyl-1H-pyrrole	51.82	81	trace
10	1-methyl-2-pyrrolidinone	60.32	99	6.66
11	1-(1-methylvinyl)pyrrolidin-2-one	60.80	125	0.34
12	1-ethyl-2-pyrrolidinone	62.11	113	2.52
13	1-(methylethyl)-3-pyrrolin-2-one	62.93	125	0.39
14	1-ethenyl-2-pyrrolidinone (monomer)	64.66	111	68.95
15	1-(methylethyl)-2-pyrrolin-5-one	66.37	125	3.70
16	1-(methylethyl)pyrrolidin-2-one	66.54	127	0.39
17	1-(1-ethylvinyl)pyrrolidin-2-one	68.81	139	0.32
18	2,6-dimethyl-4-pyridinol ?	71.45	123	0.66
19	1-(1-methylvinyl)-2-pyrrolidinone	74.45	125	1.50
20	2-pyrrolidinone	79.59	85	12.57
21	1-(1-ethylvinyl)-3-pyrrolin-2-one	81.78	137	0.68
22	analog of 1-(1-ethylvinyl)-3-pyrrolin-2-one	86.35	137	0.83
23	1-(1-propylvinyl)-3-pyrrolin-2-one	87.25	151	trace
24	1-[3-(2-oxopyrrolidinyl)but-3-enyl]pyrrolidin-2-one	96.85	222	0.48

Some of the peak identifications given in Table 6.5.13 are tentative only. For example, the spectrum for 1-(1-methylvinyl)-2-pyrrolidinone is not available in common mass spectral libraries. The tentatively assigned spectrum for this substance is shown in Figure 6.5.15.

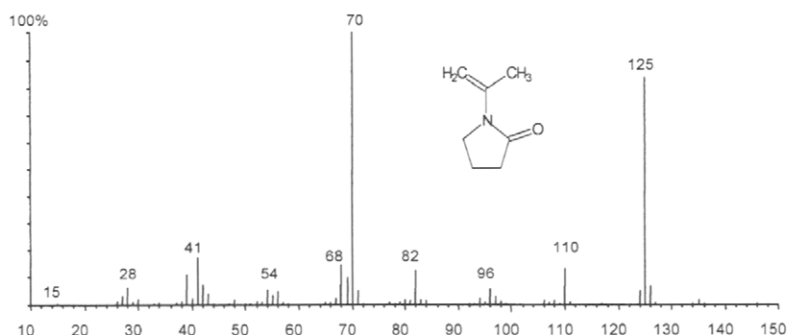


FIGURE 6.5.15. Mass spectrum tentatively assigned to 1-(1-methylvinyl)-2-pyrrolidinone.

As seen from Figure 6.5.14 and Table 6.5.13, PVP generates by pyrolysis a significant level of monomer, but also some 2-pyrrolidinone. A combined process including the elimination of the side substituent as well as cleavage of the polymeric chain with the formation of monomer occurs in the pyrolysis conditions previously described [41].

Similar to vinyl derivatives, a number of substituted vinylidene polymers are used in practice. Some of these polymers are part of classes of polymers such as halogenated polyolefins and were discussed separately (see Section 6.3 and 7.5). One example of polymer that can be indicated here is poly(vinylidene cyanide). Its pyrolysis generates a high yield of monomer [42].

- Copolymers of various vinyl derivatives

Vinyl derivatives are frequently used to obtain copolymers. Some of the copolymers containing vinyl comonomers are discussed in other sections of this book in connection with the pairing comonomer, or in the sections dealing with halogenated copolymers or the copolymers of acrylates and methacrylates.

Vinyl copolymers substituted with -OH, -O-R, -OC(O)-R, -C(O)-R, or -C₅H₄N groups have various practical applications, depending on their composition. These applications include uses in glues, lacquers, protective films, flocculent agents, various formulations in cosmetics (e.g. poly(1-vinyl-2-pyrrolidinone-co-ethyl methacrylate-co-methacrylic acid) is used in hair spray formulations, poly(1-ethenyl-2-pyrrolidinone-co-1-eicosene) is used as a pigment dispersant in cosmetics), etc. A number of pyrolysis studies were done on these materials [43], etc. Some thermal properties of a few common vinyl copolymers are summarized in Table 6.5.14.

TABLE 6.5.14. Summary regarding literature on thermal decomposition of several vinyl copolymers [13].

Polymer	Temp. °C	Results	Ref.
poly(vinyl acetate- <i>alt</i> -maleic anhydride)	ambient to 500	acetic acid, CO ₂ , H ₂ O, maleic anhydride, CO	44
poly(vinyl acetate-co-methyl methacrylate)	250–350	acetic acid and methyl acetate from side group eliminations; the methyl acetate level is higher than in PMMA homopolymer	11
poly(vinyl acetate- <i>alt</i> -crotonic acid)	ambient to 500	ethene, propene, acetic acid, CO ₂ , propanoic acid, 2-methylpropanoic acid, butanoic acid, cyclopentanone, some unsaturated cyclic and acyclic aliphatic ketones, some chain fragments containing lactones	45
poly(vinyl acetate- <i>alt</i> -methyl-vinylidene cyanide) with 10-15 mol% VA homosequence	285–350	vinyl acetate, acetonitrile, HCN, acetic acid, acetamide, 2-methyl-1-aminonaphthalene, 3-cyano-3-pentene	46
poly(vinyl acetate-co-vinyl alcohol) 50-99 mol% VAL	ambient to 600	acetaldehyde, acetone, benzene, crotonaldehyde, acetic acid	1
poly(N-vinyl-pyrrolidone-co-acrylic acid)	above 250	H ₂ O, CO ₂ , decarboxylation more rapid than poly(acrylic acid)	47

TABLE 6.5.14 (continued). Summary regarding literature on thermal decomposition of several vinyl copolymers [13].

Polymer	Temp. °C	Results	Ref.
poly(2-vinyl-naphthalene-co-methylacrylate)	400	random cleavage, methanol, lactone	48
poly(2-vinyl-naphthalene- <i>alt</i> -methylmaleate)	390	random cleavage	48
poly(N-vinyl-pyrrolidone-co-vinyl acetate)	432	60% weight loss for 10% VA	49

Examples of pyrolysis results for copolymers of vinyl derivatives (not including acrylates, methacrylates, or halogenated vinyl derivatives) were discussed in Section 6.1 for poly(ethylene-co-vinyl acetate) $(-\text{CH}_2\text{CH}_2-)_x[\text{CH}_2\text{CH}(\text{OOCCH}_3)-]_y$ (see Fig. 6.1.12), in Section 6.3 for poly(vinyl chloride-co-vinyl acetate) 86 wt % vinyl chloride $[-\text{CH}_2\text{CH}(\text{Cl})-]_x[-\text{CH}_2\text{CH}(\text{COOCH}_3)-]_y$ (see Fig. 6.3.3), and in Section 6.2 for poly(2-vinylpyridine-co-styrene) styrene 30% $[-\text{CH}_2\text{CH}(2-\text{C}_5\text{H}_4\text{N})-]_x[-\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)-]_y$ (see Fig. 6.2.11) and for poly(vinylpyrrolidone-co-styrene) (see Fig. 6.2.14).

References 6.5

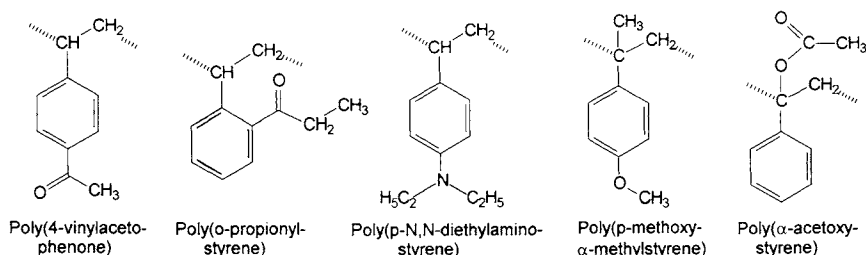
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6.6 POLY(STYRENES) WITH VARIOUS NON-HYDROCARBON TYPE SUBSTITUENTS

- General aspects

Poly(styrenes) and poly(α -substituted styrenes) can bear various substituents on the aromatic ring. These substituents may affect other properties of the polymer, but their thermal stability is not very different from that of unsubstituted poly(styrene). Some of the idealized structures of the polymers in this group are shown below:



Various studies regarding thermal decomposition of the polymers from this class are reported in literature [1]. Some results are summarized in Table 6.6.1.

TABLE 6.6.1. Summary regarding literature information on thermal decomposition of several substituted styrene polymers.

Polymer	Temp. °C	Results	Ref.
poly(4-vinylacetophenone)	380	CO, CH ₄ , ethane, 4-acetylstyrene, 4-acetyltoluene, styrene, toluene, 4-vinylacetaldehyde, α -methylstyrene, α -methyl-4-acetylstyrene, 4-methylstyrene	2
poly(α -acetoxy-styrene)	270	acetic acid (99%), mixture of α -acetoxy-styrene and acetophenone (1%)	3
poly(α -acetoxy-styrene)	200 and 220	two steps of degradation, one between 140° C and 200° C, the second above 220° C	4
poly(<i>m</i> -amino-styrene)	340–500	gaseous fraction CO ₂ , CH ₄ , C ₂ H ₆ , C ₃ H ₆ , C ₃ H ₈ ; liquid fraction <i>m</i> -aminostyrene, <i>m</i> -toluidine; gum fraction mainly dimer and trimer; crosslinked residue remains	5
poly(<i>m</i> -amino-styrene)	320–500	monomer yield rises from 41% (320° C) to 61% (500° C); minor product is <i>m</i> -toluidine, with traces of aniline, <i>m</i> -ethylaniline, α -methyl- <i>m</i> -aminostyrene, H ₂ , CO ₂ , CH ₄ ; remainder comprises chain fragments and residue	6
poly(<i>m</i> -N,N-dimethylamino-styrene)	350–500	<i>m</i> -N,N-dimethylaminostyrene, N,N-dimethyl- <i>m</i> -toluidine, <i>m</i> -xylene, styrene, N,N-dimethyl- <i>m</i> -ethylaniline, toluene, <i>m</i> -methylstyrene, α -methyl- <i>m</i> -N,N-dimethylaminostyrene, <i>trans</i> - β -methyl- <i>m</i> -N,N-dimethylaminostyrene, α -ethyl- <i>m</i> -N,N-dimethylaminostyrene, N-methyl- <i>m</i> -toluidine, N-methyl- <i>m</i> -ethylaniline, N-methyl- <i>m</i> -aminostyrene, oligomers of <i>m</i> -N,N-dimethylaminostyrene and related compounds	7, 8
poly(<i>m</i> -N,N-dimethylamino-styrene)	500 for 30 min.	N,N-dimethylaniline (0.2% of original polymer weight), N,N-dimethyl- <i>p</i> -toluidine (2.8%), N-methylaniline (0.4%), N,N-dimethyl- <i>p</i> -ethylaniline (0.4%), N-methyl- <i>p</i> -toluidine (0.4%), N-methyl- <i>o</i> -toluidine (0.4%), <i>p</i> -toluidine (0.4%), N-methyl- <i>p</i> -ethylaniline (0.4%), <i>p</i> -N,N-dimethylaminostyrene (36.3%), α -methyl- <i>p</i> -N,N-dimethylaminostyrene (0.7%)	9
poly(<i>o</i> -propionyl-styrene)	385	CO, CH ₄ , ethane, ethene, butane, 2-propionylstyrene, 2-propionyltoluene, styrene, toluene, α -methylstyrene, α -methyl-2-propionylstyrene, various dimeric and trimeric species not fully characterized	10
poly(<i>p</i> -N,N-diethylamino-styrene)	350–500	toluene, styrene, <i>p</i> -ethylstyrene, N,N-diethyl- <i>p</i> -toluidine, N,N-diethyl- <i>p</i> -ethylaniline, <i>p</i> -N,N-diethylaminostyrene, α -methyl-N,N-diethylaminostyrene, 2-(<i>p</i> -N,N-diethylaminophenyl)butane, α -propyl- <i>p</i> -N,N-diethylaminostyrene, N-ethyl- <i>p</i> -toluidine, N-ethyl- <i>p</i> -ethylaniline, N-ethyl- <i>p</i> -aminostyrene and closely related compounds	11, 12
poly(styrene peroxide)	60–70	kinetic study of decomposition at different temperatures	13

One polymer from this class that has been studied by Py-GC/MS is poly(4-vinylphenol) or poly(4-hydroxystyrene), CAS# 24979-70-2, with the idealized structure $[\text{CH}_2\text{CH}(\text{p-C}_6\text{H}_4\text{OH})]_n$. The results are shown in Figure 6.6.1. The pyrolysis was done similarly to other polymers previously discussed in this book at 600° C in He with the separation on a Carbowax column (see Table 4.2.2) and with MS detection. The peak identification for the chromatogram was done using MS spectral library searches and is given in Table 6.6.2.

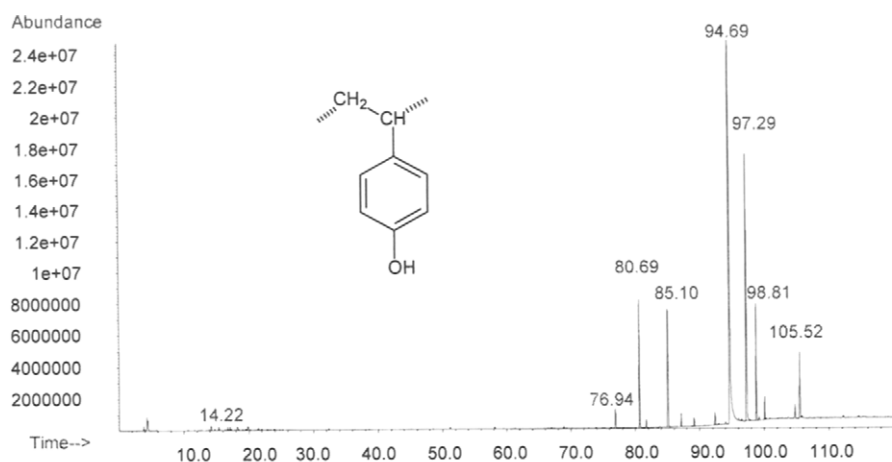


FIGURE 6.6.1. Result for a Py-GC/MS analysis of poly(4-vinylphenol) $M_w = 8000$. Pyrolysis done at 600°C in He, with the separation on a Carbowax type column.

TABLE 6.6.2. Compounds identified in the pyrogram of poly(4-vinylphenol) shown in Figure 6.6.1.

Peak	Compound	Ret. Time	MW	Area %
1	2-methylpropane	4.35	58	1.42
2	2-methylpropene	4.45	56	trace
3	1-butene	4.55	56	trace
4	acetaldehyde	5.85	44	trace
5	2,2,5-trimethylhexane ?	14.22	128	trace
6	3,7-dimethylnonane ?	15.38	156	trace
7	5-ethyl-2,2,3-trimethylheptane ?	16.77	170	trace
8	2,2,7,7-tetramethyloctane ?	17.12	170	trace
9	water	18.23	18	trace
10	2,2,6-trimethyldecane	19.09	184	trace
11	phenol	76.94	94	1.23
12	4-methylphenol	80.69	108	8.21
13	1-(2,4,5-trimethylphenyl)ethanone	81.75	162	0.49
14	4-ethylphenol	85.10	122	7.49
15	4-(1-methylethyl)phenol	87.16	136	0.75
16	4-propylphenol	89.16	136	0.48
17	4-(2-propenyl)phenol	92.40	134	0.70
18	4-vinylphenol	94.69	120	46.94
19	4-(1-methylvinyl)phenol	97.29	134	18.92
20	2-hexylphenol	98.82	178	6.77
21	?-(2-propenyl)phenol	100.09	134	1.28
22	4-(hept-?-enyl)-phenol	104.76	190	1.05
23	4-(hex-?-enyl)-phenol	105.52	176	4.27

Poly(4-vinylphenol) gives by pyrolysis a proportion of monomer lower than polystyrene. The dimer, if formed from the pyrolysis, is not seen in the pyrogram since the chromatographic conditions are not appropriate for its elution. However, the pyrolysis mechanism for poly(4-vinylphenol) is very likely similar to that of polystyrene.

Off-line pyrolysis of a poly(4-vinylphenol) sample followed by the silylation using N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) of the pyrolysate and GC/MS analysis with separation on a DB5 column (30 m length, 0.32 mm i.d., 0.32 μ m film thickness) is shown in Figure 6.6.2. The identification of the compounds in the silylated pyrolysate was done using MS library searches and is given in Table 6.6.3

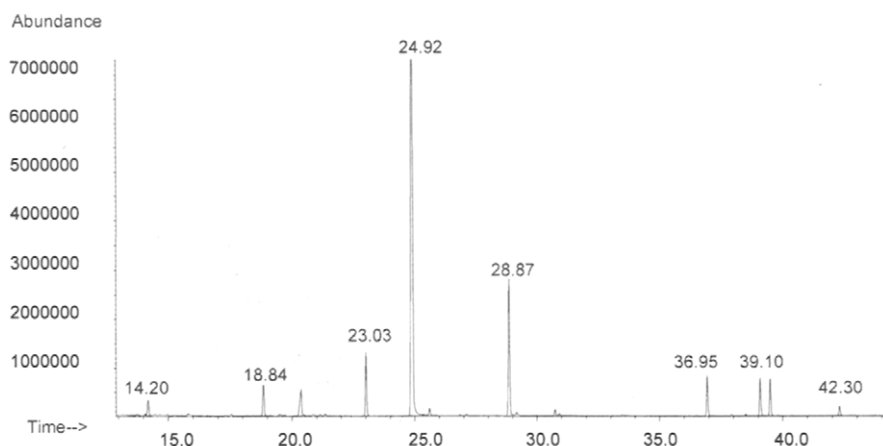


FIGURE 6.6.2. Result for a off-line pyrolysis of a poly(4-vinylphenol) $M_w = 8000$ followed by silylation and GC/MS analysis. Pyrolysis done at 600° C in He, with the separation on a 5% phenyl methylsilicone column.

TABLE 6.6.3. Compounds identified in the pyrogram obtained off-line from poly(4-vinylphenol) after silylation with BSTFA and shown in Figure 6.6.2.

Peak	Compound	Ret. Time	MW	Area %
1	phenol TMS*	14.20	166	1.64
2	4-methylphenol TMS	18.84	180	2.69
3	compound from the reagent	20.36		3.83
4	3,5-dimethylphenol TMS	23.03	194	5.57
5	4-ethenylphenol TMS	24.92	192	60.86
6	4-isopropylphenol TMS	25.61	208	0.82
7	4-(1-methylvinyl)phenol TMS	28.87	206	12.15
8	resorcinol 2-TMS	30.74	254	0.81
9	2-hexylphenol TMS	36.95	250	3.72
10	4-(hex-?-enyl)-phenol TMS ?	39.10	248	3.67
11	internal standard	39.50		3.39
12	3-(p-trimethylsilyloxyphenyl)-1-trimethylsilyloxypropane ?	42.30	296	0.86

*Note: TMS indicates trimethylsilyl ether.

The comparison of the list of compounds from Table 6.6.3 with that from Table 6.6.2 shows that the compounds identified after silylation are practically the same as the compounds identified by on-line Py-GC/MS. Except for resorcinol and 3-(p-hydroxyphenyl)propane-1-ol (tentatively identified), no larger molecules are seen in the pyrolysate by using silylation.

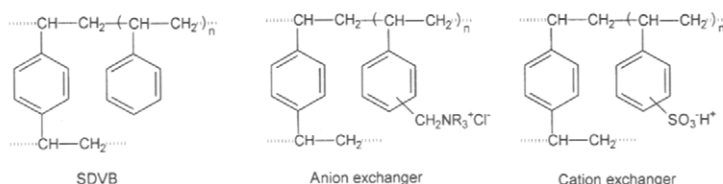
An important group of substituted polystyrenes is that with ionic groups as substituents. The backbones of these polymers have covalently bound groups that are able to exist in ionic form. The presence of the ionic groups provides properties of ion exchanger, and the resins act as polyelectrolytes. Some of the groups introduced in polystyrene type ion exchangers are indicated in Table 6.6.4.

TABLE 6.6.4. Functional groups introduced in polystyrene type ion exchange resins.

Type	Functional group	Type	Functional group
<i>Cation exchangers</i>		<i>Anion exchangers</i>	
sulfonic acid	$-\text{SO}_3^-\text{H}^+$	quaternary amine	$-\text{N}(\text{CH}_3)_3^+\text{OH}^-$
carboxylic acid	$-\text{COO}^-\text{H}^+$		$-\text{N}(\text{CH}_3)_2(\text{CH}_2\text{CH}_2\text{OH})^+\text{OH}^-$
phosphonic acid	$-\text{HPO}_2^-\text{H}^+$	tertiary amine	$-\text{NH}(\text{CH}_3)_2^+\text{OH}^-$
phosphinic acid	$-\text{HPO}_2^-\text{H}^+$	secondary amine	$-\text{NH}_2(\text{CH}_3)^+\text{OH}^-$
phenolic	$-\text{C}_6\text{H}_4-\text{O}^-\text{H}^+$	primary amine	$-\text{NH}_3^+\text{OH}^-$
arsonic acid	$-\text{HAsO}_3^-\text{H}^+$	sulfides	$=\text{S}^+\text{OH}^-$
selenonic acid	$-\text{SeO}_3^-\text{H}^+$		
phenoxy group	$-\text{C}_6\text{H}_4-\text{O}^-\text{H}^+$		

In addition to the functionalities attached to the benzene ring in polystyrene, it is also possible to include in the polystyrene backbone different monomer units and generate solid phase sorbents with modified properties. It is common, for example, that the ion exchangers or solid phase sorbents contain a certain proportion of divinylbenzene (DVB) used for crosslinking the polystyrene macromolecules. Contents around 8–12% DVB in styrene are common in commercial products. Other cross-linking substances can be used besides divinylbenzene, such as ethylenedimethacrylate.

The ion exchange resins can be obtained either from the polymerization of substituted styrene or by the chemical modification of the polymer. For example, styrene/divinylbenzene (SDVB) polymer can be modified by chloromethylation (using HCl and formaldehyde in the presence of ZnCl_2) followed by reaction with a tertiary amine. This derivatization leads to a strong anion exchange material. Sulfonation of SDVB leads to a strong cation exchanger. The idealized structure of SDVB and of the anion and cation exchangers obtained from this material are shown below:



Other groups can be included in the SDVB backbone by copolymerization.

The pyrogram of a sample of poly(4-styrenesulfonic acid) performed at 600°C in He and with the separation done on a Carbowax column (similar to other examples, e.g. polyethylene) is shown in Figure 6.6.3. The peak identification for the chromatogram shown in Figure 6.6.3 was done using MS spectral library searches and is given in Table 6.6.5.

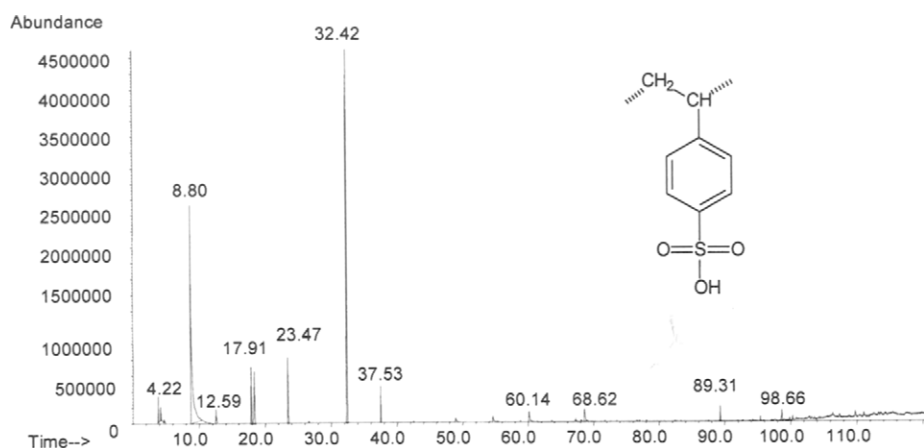


FIGURE 6.6.3. Result for a Py-GC/MS analysis of poly(4-styrenesulfonic acid). Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 6.6.5. Compounds identified in the pyrogram of poly(4-styrenesulfonic acid) as shown in Figure 6.6.3.

Peak	Compound	Ret. Time	MW	Area %
1	ethene	4.22	28	0.27
2	hydrogen sulfide	4.72	34	0.55
3	sulfur dioxide	8.80	64	35.02
4	benzene	12.59	78	1.74
5	toluene	17.91	92	5.50
6	water	18.42	18	6.87
7	ethylbenzene	23.47	106	5.66
8	styrene	32.42	104	31.01
9	α -methylstyrene	37.53	118	3.53
10	1-propenylbenzene	42.51	118	trace
11	benzenethiol	48.86	110	trace
12	4-methylbenzenethiol	54.63	124	1.38
13	1-methyl-2(methylthio)benzene	60.14	138	2.23
14	naphthalene	63.61	128	trace
15	benzo[b]thiophene	67.30	134	trace
16	ethenylthiobenzene	68.10	136	trace
17	2,3-dihydrobenzo[b]thiophene	68.62	136	2.73
18	1-methylnaphthalene	71.71	142	trace
19	3-methylbenzo[b]thiophene	73.50	148	trace
20	1,1'-(1,3-propanediyl)bis-benzene	89.31	196	1.70
21	1,1'-cyclopropylidenebis-benzene	98.66	194	1.32
22	1,1'-(1,2-ethenediyl)bis-benzene	100.31	180	0.50

When the separation of the pyrolysis products is done on a polar column (Carbowax), strongly polar compounds such as 5-styrenesulfonic acid are not likely to elute. The separation of ionic or strongly polar compounds from the pyrolysates must be done either on a different column or after derivatization.

Substituted styrenes are also included in a number of copolymers. Frequently, these copolymers use styrene or divinylbenzene as the other comonomer. Some copolymers of substituted styrenes were already discussed in Section 6.2 (see Figures 6.2.5 through 6.2.16).

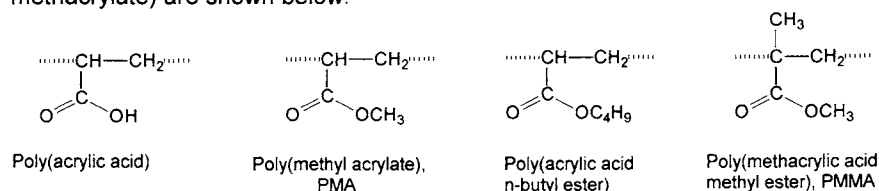
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6.7 ACRYLIC ACID AND METHACRYLIC ACID DERIVATIVES

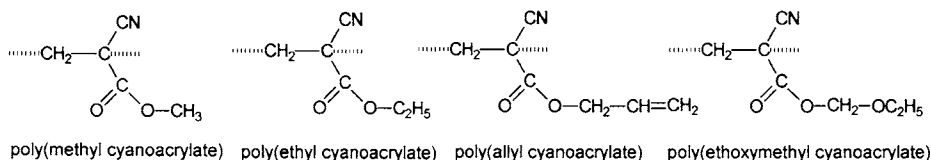
- General aspects

Poly(acrylates) and poly(methacrylates) form another class of common polymers with saturated carbon chain backbone. Polyacrylates can be considered vinyl polymers with the -COOR group attached at every other carbon atom in the chain. However, due to their common use and particular properties, polyacrylates form a separate polymer class together with polymethacrylates. Among the most common polymers from this class are those obtained from acrylic acid methyl ester (PMA) and methylacrylic (methacrylic) acid methyl ester (PMMA). Acrylic polymers have many practical applications in automotive industry, in the production of medical materials, paints, coatings and lacquers, adhesives, textiles, and synthetic leather. Poly(methacrylic acid methyl ester) can be obtained in cast sheets with applications in technical components, furniture, building materials, etc. Formulas for poly(acrylic acid), two polyacrylates, and poly(methyl methacrylate) are shown below:



The carboxyl group in acrylates and methacrylates can be esterified with various other alcohols, including diols such as ethylene glycol, diethyleneglycol, etc. In addition to the free acids and their esters, to this class can be added other derivatives of acrylic acid such as poly(acrylonitrile) $[-\text{CH}_2-\text{CH}(\text{CN})-]_n$, poly(acrylamide) $[-\text{CH}_2-\text{CH}(\text{CONH}_2)-]_n$,

poly(acryloyl chloride) $[-CH_2-CH(C(O)Cl)-]_n$, and some compounds with two functional groups on the carbon chain such as poly(α -chloro-acrylonitrile) $[-CH_2-C(Cl)(CN)-]_n$, poly(α -phenyl-acrylonitrile) $[-CH_2-C(C_6H_5)(CN)-]_n$, etc. as well as several cyanoacrylates commonly used in adhesive formulations with structures shown below:



Cyanoacrylates undergo easily anionic polymerization in the presence of weak bases, including H_2O . They are used in commercial products (Super glue) mixed with traces of acidic stabilizers, which are neutralized in contact with various surfaces during the use.

Acrylates are obtained by several procedures, typically by polymerization in solution or in suspension using an initiator such as peroxide or AIBN (2,2'-azobisisobutyronitrile). Bulk polymerization also can be used for certain polymers when a partial polymerization is initially performed, followed by the completion of the polymerization in the desired shape of the final object. Since acrylates are typically obtained by free radical initiation, the common form of these polymers is atactic, although the stereoregular materials are known. The polymerization of acrylates usually takes place in head to tail form (H-T), and most acrylates are found in this form.

- Poly(acrylic acid)

Poly(acrylic acid), CAS# 9003-01-4, is a polymer soluble in water and in some alcohols, behaving as a polyelectrolyte. The solubility decreases from the linear polymer toward cross-linked polymer, and because most applications of the poly(acrylic acid) require solubility, the linear polymer is more frequently used in practice. The linear polymer can be prepared from 20–30% solutions by free radical polymerization (higher concentrations leading to cross-linking). Various salts of the polymer (sodium, potassium, ammonium) can form water solutions with high viscosities. These salts are used as thickeners in cosmetics, creams, lotions, hair preparations, pigments, polishing agents and emulsions. The polyelectrolyte properties of the polymer are used in making ion exchange resins, flocculating agents, detergents, dispersants, and sludge conditioners for water treatment. Other applications include paper sizing, wrap sizing for nylon fibers, adhesives, control release coatings for drug delivery of tablets, etc.

When heated, the polymer starts decomposing at about $250^\circ C$. The TGA curve for a poly(acrylic acid) sample with $M_w = 1,000,000$ is shown in Figure 6.7.1. The heating was done in air between $30^\circ C$ and $830^\circ C$ at a rate of $10^\circ C/min$. The first step of weight loss is due to the evaporation of moisture from the sample. A complex decomposition pattern is further indicated by the TGA, the loss of about 77.7% (after correction for the adsorbed water loss), or the curve inflection at about $350^\circ C$ not corresponding to an assignable decomposition reaction. The losses are at least in part caused by the elimination of CO_2 , water or of both. However, CO_2 accounts for 61% of the MW of the monomer, and H_2O for 25%.

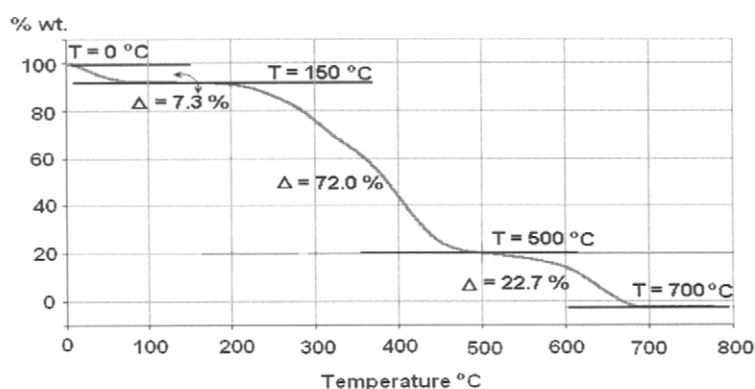


FIGURE 6.7.1. Variation of weight % loss for a poly(acrylic acid) sample in a TGA experiment at a heating rate of 10°C/min .

Several studies on thermal degradation of poly(acrylic acid) and of its salts are reported in literature [1–5]. Some results from these studies are summarized in Table 6.7.1 [6].

TABLE 6.7.1. Summary regarding reports on thermal decomposition of poly(acrylic acid) and of some of its salts.

Polymer	Temp. $^{\circ}\text{C}$	Results	Ref.
poly(acrylic acid calcium salt)	ambient to 500	CO , CH_4 , CO_2 , acetone, ketene, ethene, propene, 1-butene, benzene, toluene, mesitylene, xylene, methyl ethyl ketone, diethyl ketone, methyl-n-propyl ketone, methyl-n-butyl ketone, ethyl vinyl ketone, methyl propenyl ketone (trace), ethyl propyl ketone (trace), 3-methyl-cyclopentanone, cyclohexanone (trace), cyclohexa-2-enone, 2-methyl-cyclohexanone, 1-methyl-cyclohexa-1-ene-3-one (trace), acrolein, mesityl oxide, ethanal, propanal, butanal, chain fragments, some monomer	7
poly(acrylic acid magnesium salt)	ambient to 500	CO , CH_4 , CO_2 , acetone, ketene, ethene, propene, 1-butene, benzene, toluene, xylene, cyclopentene, methyl ethyl ketone, diethyl ketone, methyl-n-propyl ketone, di-n-propyl ketone, methyl vinyl ketone, methyl isopropenyl ketone, methyl isopropyl ketone, ethyl vinyl ketone, trace amounts of methyl-n-butyl ketone, cyclopentanone, cyclohexanone, acrolein, ethanal, butanal, chain fragments, some monomer	7
poly(acrylic acid potassium salt)	ambient to 500	CO , CH_4 , CO_2 , ketene, 1-butene, propene, acetone, methyl ethyl ketone, methyl n-propyl ketone, 1,4-cyclohexadiene, toluene, 1-methyl-1,3-cyclohexadiene, 2-hexanone, cyclopentene, 1-methyl cyclopentene, mesityl oxide, xylenes, benzene, ethene, cyclopentanone, 1,3-cyclopentadiene, diethyl ketone, short chain fragments, traces of monomer	8
poly(acrylic acid sodium salt)	ambient to 500	CO , CH_4 , CO_2 , ketene, 1-butene, propene, acetone, methyl ethyl ketone, methyl isopropyl ketone, methyl-n-propyl ketone, diethyl ketone, methyl propenyl ketone, 3-hexanone, toluene, 2-hexanone, 1,3-cyclopentadiene, cyclopentanone, 2-methylcyclopentanone, mesityl oxide, xylenes, benzene, propionaldehyde, acrolein, acetaldehyde, ethene, short chain fragments, traces of monomer	8
poly(acrylic acid)	ambient to 500	CO , CO_2 , H_2O , CH_4 , acetone, ketene, ethene, propylene, 1-butene, methyl vinyl ketone, benzene, acrylic acid, toluene, xylene, short chain fragments such as dimer to octamer with unsaturated and anhydride functionalities	9

The results for a Py-GC/MS analysis of a sample of poly(acrylic acid) with $M_w = 1,000,000$ are shown in Figure 6.7.2. The pyrolysis was done at 600° C in He at a heating rate of 20° C/ms. The separation was done on a Carbowax column (60 m, 0.32 mm i.d., 0.32 μ m film thickness) with the GC starting at 40° C with a ramp of 2° C/min. up to 240° C and a final oven time of 20 min. (see Table 4.2.2). The MS was operated in EI+ mode. The peak identification for the chromatogram was done using MS spectral library searches only and it is given in Table 6.7.2.

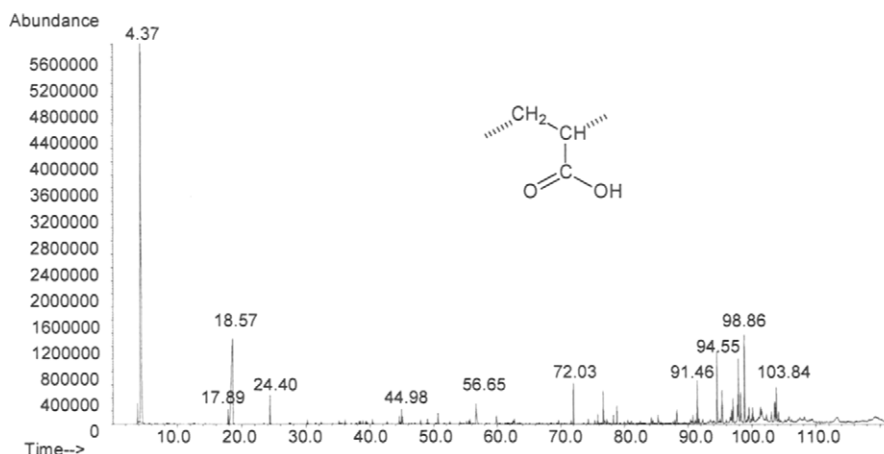


FIGURE 6.7.2. Result for a Py-GC/MS analysis of poly(acrylic acid) $M_w = 1,000,000$. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 6.7.2. Compounds identified in the pyrogram of poly(acrylic acid) $M_w = 1,000,000$ shown in Figure 6.7.2.

Peak	Compound	Ret. Time	MW	Area %
1	carbon dioxide	4.37	44	40.46
2	toluene	17.89	92	0.84
3	water	18.57	18	15.12
4	1,2-dimethylbenzene	24.40	106	1.51
5	1,4-dimethylbenzene	27.38	106	trace
6	cyclopentanone	27.79	84	
7	1-ethyl-3-methylbenzene	30.20	120	trace
8	1,3,5-trimethylbenzene	31.51	120	trace
9	styrene	32.51	104	trace
10	1-ethyl-4-methylbenzene	34.12	120	trace
11	cyclohexanone	35.15	98	trace
12	2-methylcyclohexanone	36.08	112	trace
13	1-ethyl-3,5-dimethylbenzene	37.07	134	trace
14	3-methylcyclohex-3-en-1-one	38.27	110	trace
15	ethenylmethylbenzene	39.32	118	trace
16	2-methyl-2-cyclopenten-1-one	40.35	96	trace
17	3,5-dimethyl-2-cyclohexen-1-one	44.59	124	trace
18	3-methyl-2-cyclohexen-1-one	44.98	110	1.23
19	acetic acid	45.12	60	trace

TABLE 6.7.2 (continued). Compounds identified in the pyrogram of poly(acrylic acid) $M_w = 1,000,000$ shown in Figure 6.7.2.

Peak	Compound	Ret. Time	MW	Area %
20	indene	47.90	116	trace
21	2,3-dihydro-4-methyl-1H-indene	49.03	132	trace
22	propanoic acid	50.67	74	trace
23	2-propenoic acid	56.67	72	2.06
24	2-methyl-2-propenoic acid	59.87	86	trace
25	1,3-dimethyl-1H-indene	62.68	144	trace
26	2-methylenebutanoic acid	66.61	100	trace
27	1-methylnaphthalene	69.70	142	trace
28	2,6-dimethylphenol	72.03	122	2.15
29	2-ethyl-5-methylphenol	74.33	136	trace
30	2,3-dihydro-2-methyl-1H-inden-1-one	75.36	146	trace
31	2,3-dihydro-3,3-dimethyl-1H-indan-1-one	75.85	160	trace
32	2-methylphenol	76.72	108	2.19
33	2,3-dihydro-1H-indan-1-one	78.30	132	trace
34	7-methylindan-1-one	78.88	146	0.93
35	5,7-dimethyl-4,4a,5,6-tetrahydro-2(3H)-naphthalenone ?	88.23	176	trace
36	4,4a,5,6-tetrahydro-2(3H)-naphthalenone / 3,4-dihydrocoumarin ?	90.75	148	trace
37	7-methyl-4,4a,5,6-tetrahydro-2(3H)-naphthalenone / 3,4-dihydro-6-methylcoumarin ?	91.46	162	2.77
38	5,7-dimethyl-3,4,5,6,7,8,4a-heptahydro-2(3H)-naphthalenone ?	94.55	178	4.87
39	3-butyl-5-methylphenol	95.36	164	2.14
40	3-ethyl-2H-1-benzopyran-2-one	97.91	174	5.03
41	2H-1-benzopyran-2-one	98.27	146	2.29
42	3-methyl-2H-1-benzopyran-2-one	98.86	160	5.63
43	9,10-dihydrophenanthren-2-ol ?	99.55	196	1.65
44	?,?-dimethyl-4,4a,5,6-tetrahydro-2(3H)-naphthalenone	100.13	176	1.81
45	?-methyl-4,4a,5,6-tetrahydro-2(3H)-naphthalenone	101.37	162	3.51
46	1,2,3,4-tetrahydrophenanthren-3-ol ?	103.59	198	1.50
47	?-methyl-9,10-dihydrophenanthren-2-ol	103.84	210	2.32

Some of the peak assignments given in Table 6.7.2 are tentative. For example, the spectrum for the peak eluting at 97.91 min. was assigned to 3-ethyl-2H-1-benzopyran-2-one by similarity to the spectrum of 3-methyl-2H-1-benzopyran-2-one available in the NIST mass spectral library. The two spectra are shown in Figure 6.7.3.

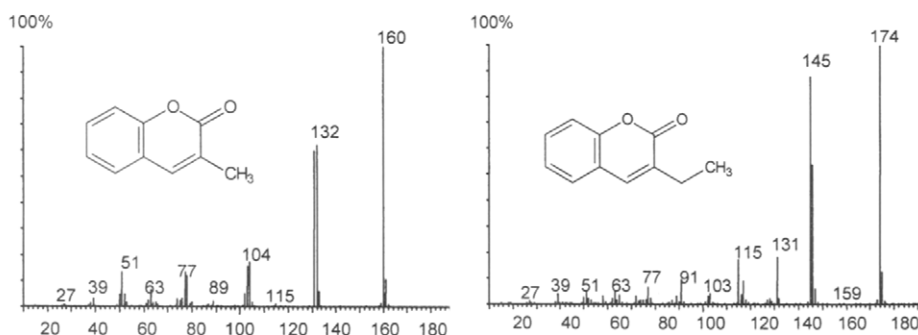
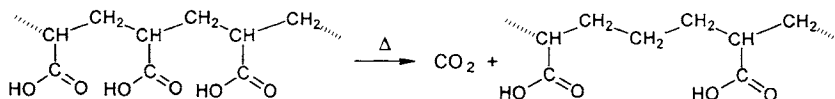
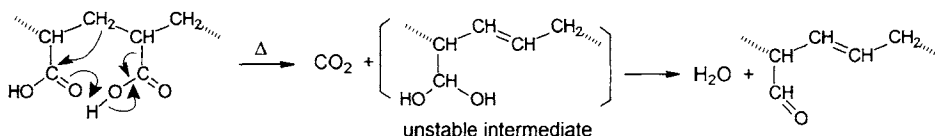


FIGURE 6.7.3. Mass spectrum of 3-methyl-2H-1-benzopyran-2-one ($MW = 160$) and that tentatively assigned to 3-ethyl-2H-1-benzopyran-2-one ($MW = 174$).

The pyrolysis products of acrylic acid indicate that only about 25% of monomer is generated during pyrolysis. A significant amount of decarboxylation takes place during pyrolysis. Also, water is present in the pyrolysate (about 15%). The elimination of CO_2 may take place as a simple reaction at the side chain of the polymer as shown below:



However, the previous reaction does not explain the formation of water, although for about 90% of the molecules of CO_2 , a corresponding molecule of water is found in the pyrolysate (some water in the pyrolysate may come from the adsorbed water on the polymer). Also, the lack of long chain hydrocarbons in the pyrolysate and the presence of aromatic compounds and of some ketones indicate that the decarboxylation process has a different mechanism. One likely possibility is the reaction involving a cyclic mechanism for the elimination of CO_2 and subsequently of H_2O , as shown below:



The presence of the double bonds in the polymer backbone and its further thermal decomposition may explain the formation of certain aromatic compounds in poly(acrylic acid) pyrolysate.

Since a number of pyrolysis products of poly(acrylic acid) are highly polar compounds (e.g. acids), the use of a Carbowax type column for the separation is not the ideal choice. Pyrolysis with methylation using "in situ" tetramethylammonium hydroxide (TMAH) is an alternative way for detecting some of the polar pyrolysis products. However, as indicated in Section 3.2, pyrolysis in the presence of a methylating reagent may not be identical to the products obtained by off-line methylation of the pyrolysis products [10]. This is the case mainly when the polymers can undergo complex reactions in the presence of a basic compound (such in the case of pyrolysis of polymeric carbohydrates in the presence of TMAH). Since poly(acrylic acid) is stable in basic conditions, the thermochemolysis is not expected. The results of pyrolysis of a poly(acrylic acid) sample in the presence of TMAH are shown in Figure 6.7.4. The pyrolysis was done at 600°C in He at a heating rate of 20°C/ms with the separation done similarly to that for poly(acrylic acid) on a Carbowax column (see Table 4.2.2). The peak identification for the chromatogram was done using MS spectral library searches only and it is given in Table 6.7.3.

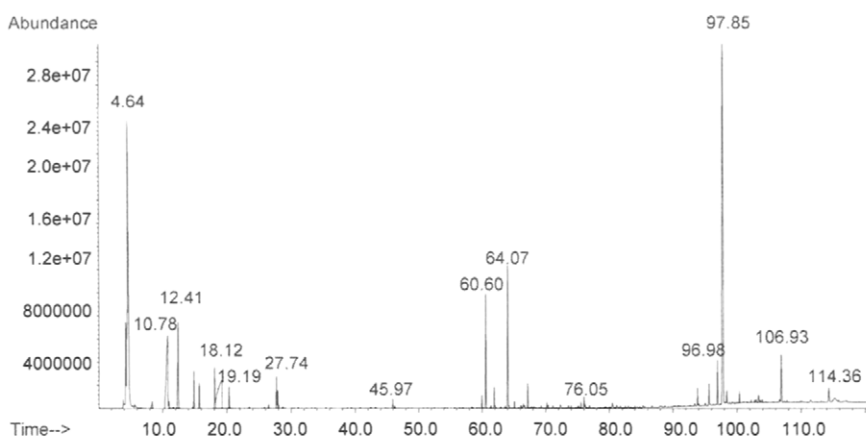


FIGURE 6.7.4. Result for a Py-GC/MS analysis of poly(acrylic acid) $M_w = 1,000,000$ in the presence of tetramethylammonium hydroxide (TMAH). Pyrolysis done on 0.4 mg material at 600°C in He, with the separation on a Carbowax type column.

TABLE 6.7.3. Compounds identified in the pyrogram of poly(acrylic acid) $M_w = 1,000,000$ in the presence of tetramethylammonium hydroxide (TMAH) as shown in Figure 6.7.4.

Peak	Compound	Ret. Time	MW	Area %
1	carbon dioxide	3.92	44	0.47
2	trimethylamine (reagent)	4.64	59	25.66
3	N,N-dimethylethanamine (from the reagent)	5.65	73	trace
4	acetic acid methyl ester	8.38		0.38
5	methanol (reagent)	10.78		8.42
6	propanoic acid methyl ester	10.98	88	trace
7	2-methylpropanoic acid methyl ester	11.68	102	trace
8	2-propenoic acid methyl ester	12.41	86	3.87
9	carbonic acid dimethylester	14.88	90	1.17
10	2-methyl-2-propenoic acid methyl ester	15.70	100	0.90
11	silicic acid tetramethyl ester (impurity)	18.12	152	1.35
12	water	19.19	18	7.76
13	2-methylenebutanoic acid methyl ester	20.37	114	0.71
14	methylenecyclopropanecarboxylic acid methyl ester	26.52	112	trace
15	N,N-dimethyl-3-methoxypropylamine (from the reagent)	27.74	117	1.05
16	N,N-dimethyl-3-methoxybutylamine (from the reagent)	27.93	131	0.64
17	unknown [58(100), 70(9), 42(6), 157 ?(2)]	45.97		0.38
18	2-methylpentanedioic acid dimethyl ester	59.99	174	0.44
19	pentanedioic acid dimethyl ester	60.60	160	4.54
20	trans-1,2-dimethyl-trans-1,2-dicarboxymethylcyclopropane	61.92	186	0.76
21	2-methylenepentanedioic acid dimethyl ester	64.07	172	6.22
22	dimethyl 2-ethylidene-5-methylpentane-1,5-dioate	65.11	200	0.23
23	1-cyclopentane-1,2-dicarboxylic acid dimethyl ester	67.20	184	0.82
24	1,2-cyclopentanecarboxylic acid dimethyl ester	70.20	186	0.39
25	2-methoxy-5-methylenehepta-2,6-dienoic acid methyl ester	75.58	182	0.19
26	2-oxo-cyclohexanecarboxylic acid methyl ester ?	76.05	156	0.52

TABLE 6.7.3 (continued). Compounds identified in the pyrogram of poly(acrylic acid) $M_w = 1,000,000$ in the presence of tetramethylammonium hydroxide (TMAH) as shown in Figure 6.7.4.

Peak	Compound	Ret. Time	MW	Area %
27	dimethyl 4-(methoxycarbonyl)-6-methyl-2-methyleneheptane-1,7-dioate	93.85	272	0.70
28	isomer of dimethyl 4-(methoxycarbonyl)-6-methyl-6-methyleneheptane-1,7-dioate	95.64	272	0.91
29	unknown [186(100), 215(72), 113(69), 85(61), 155(56)]	96.98		1.63
30	dimethyl 4-(methoxycarbonyl)-2-methyleneheptane-1,7-dioate (trimer of methyl acrylate)	97.85	258	26.95
31	dimethyl 4-(methoxycarbonyl)-2,6-dimethylene-1,7-dioate	106.93	270	2.18
32	$C_{14}H_{26}O_4$?	114.36	258	0.76

A number of substances from the pyrolysate in the presence of TMAH are methylated compounds corresponding to nonmethylated molecules in the pyrolysate of pure (with no TMAH) poly(acrylic acid). (The pyrogram of poly(acrylic acid) is shown in Figure 6.7.2.). The list of compounds that were methylated includes acetic acid, propanoic acid, 2-propenoic acid, 2-methyl-2-propenoic acid, and 2-methylenebutanoic acid. Some other compounds are identifiable as methyl esters although they were not seen in the pyrogram of poly(acrylic acid) because they are not eluted as free acids from the Carbowax column. One additional observation is that the pyrogram after methylation shown in Figure 6.7.4 and that of poly(methyl acrylate) given in Figure 6.7.7 show high similarity. This indicates that pyrolysis mechanisms of poly(acrylic acid) and of poly(methyl acrylate) are very similar.

A positive identification of the peaks in the pyrogram of poly(acrylic acid) in the presence of TMAH encounters some difficulties since many higher molecular weight compounds are not found in commercial mass spectral libraries (NIST 2002, Wiley 7, etc.). For example, this is the case of the spectrum corresponding to the main peak in the chromatogram from Figure 6.7.4, eluting at 97.85 min. The spectrum was tentatively identified as corresponding to dimethyl 4-(methoxycarbonyl)-2-methyleneheptane-1,7-dioate with MW = 258 (trimer of methyl acrylate) and is shown in Figure 6.7.5.

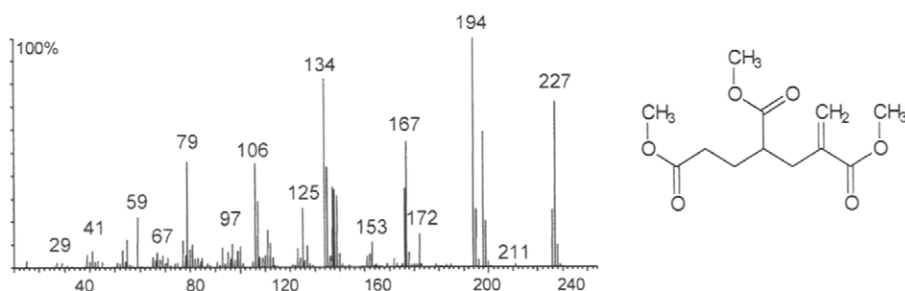


FIGURE 6.7.5. Tentatively assigned spectrum for dimethyl 4-(methoxycarbonyl)-2-methyleneheptane-1,7-dioate (trimer of methyl acrylate), MW = 258.

The assignment was based on the m/z values of different fragments (e.g., the ion $m/z = 227$ corresponds to a loss of CH_3O- , the ion $m/z = 199$ corresponds to the loss of

-COOCH₃, etc.) and on the comparison of the unknown spectrum with that of dimethyl 2-methoxycarbonyl-4-methylenepentane-1,5-dioate, which is available in Wiley4 library. This spectrum is shown in Figure 6.7.6, and the similarity between the two spectra (with a mass difference of 28 a.u for -(CH₂)₂- between the corresponding ions) is very high.

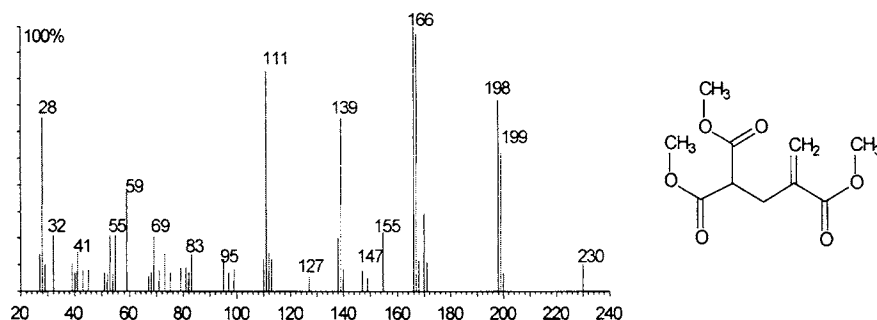


FIGURE 6.7.6. Mass spectrum of dimethyl 2-methoxycarbonyl-4-methylenepentane-1,5-dioate MW =230 available in Wiley4 commercial mass spectra library.

Py-GC/MS is not the only technique used for the detection and characterization of acrylic acid polymers. A technique used for the same purpose is pyrolysis mass spectrometry (Py-MS). As discussed in Section 3.2, in Py-MS the fragment molecules from the polymer pyrolysis are further fragmented by the electron impact in the MS with EI⁺ ionization, leading to complicated spectra. In order to diminish the excessive fragmentation incurred on pyrolysate molecules by the electron impact of the mass spectrometer, chemical ionization mass spectrometry (CI-MS, with isobutane reagent gas) was found to provide better results. This technique has been applied successfully in the analysis of pyrolysates of polymers of acrylic acid and alkyl acrylates [11]. An additional technique used for the analysis of lower molecular weight acrylic acid-containing polymers is pyrolysis at lower temperature (leading to moderately large fragments) followed by MALDI-MS analysis of PAA pyrolysate.

- Poly(acrylic acid esters)

The most common polymers from the group of poly(acrylic acid esters) are poly(methyl acrylate) (PMA) CAS# 9003-21-8, poly(ethyl acrylate) CAS# 9003-32-1, poly(butyl acrylate) CAS# 9003-49-0, and poly(2-ethylhexyl acrylate) CAS# 9003-77-4. These materials can be found in many consumer products starting with automotive parts, paints and lacquers [12–21], adhesives, or are present in fibers as copolymers [22]. The glass transition point of these materials decreases as the number of carbons in the alcohol increases. Thermal stability and pyrolysis products of polyacrylates have been thoroughly studied [23–29]. Some literature results regarding thermal decomposition of poly(acrylic acid esters) are summarized in Table 6.7.4 [6].

TABLE 6.7.4. Summary regarding literature information on thermal decomposition of poly(acrylic acid esters).

Polymer	Temp. °C	Results	Ref.
poly(acrylic acid 1,1,5-trihydro-perfluoro-amy ester)	300–315	oligomers, 1,1,5-trihydroperfluoroamyl alcohol, monomer, 1,1,5-trihydroperfluoroamyl methacrylate	30
poly(acrylic acid 2,2,2-trichloroethyl ester)	319	2,2,2-trichloroethanol (80%), monomer (9%), 1,1-dichloroethene, 2-chloroethanal, 2,2-dichloroethanal, 1,1-dichloropropane, 1,1,1-trichloroethane, 2,2,2-trichloroethyl ethanoate, 2,2,2-trichloroethyl chloromethanoate, 2,2,2-trichloroethyl propanoate, 2,2,2-trichloroethyl methacrylate, 2,2,2-trichloroethyl chloroethanoate, 2,2,2-trichloroethyl-2-chloro acrylate	31
poly(acrylic acid 2-ethyl hexyl ester)	300–500	CO ₂ , 2-ethyl-1-hexene, 2-ethyl-1-hexanol	32
poly(acrylic acid α -bromomethyl ester)	110–150	methylbromide, hydrogen bromide	33
poly(acrylic acid α -bromomethyl ester)	600	CO ₂ , propene, methyl bromide, vinyl bromide	34
poly(acrylic acid α -chloro-sec-butyl ester)	190	sec-butyl chloride, butylene, hydrogen chloride	35
poly(acrylic acid α -chloromethyl ester)	600	CO ₂ , propene, methyl chloride, monomer	36
poly(acrylic acid α -cyanomethyl ester)	>180	some monomer	37
poly(acrylic acid α -phenylmethyl ester)	210–280	monomer is the sole product	38
poly(acrylic acid benzyl ester)	260–300	major products are benzyl alcohol, chain fragments, partially crosslinked residue; minor products are CO ₂ , toluene CO, CH ₄ , H ₂	39
poly(acrylic acid benzyl ester)	unspec.	CO ₂ , benzyl alcohol, and low polymers	39
poly(acrylic acid ethyl ester)	300–500	major products, CO ₂ , ethylene, ethanol, and chain fragments; minor products, ethane, ethyl acrylate, and ethyl methacrylate	32
poly(acrylic acid ethyl ester)	ambient to 500	ethylene, CO ₂ , trace of ketene, ethanol (major product), various ethyl esters	40
poly(acrylic acid isopropyl ester)	250–500	major products CO ₂ , propene; minor products isopropanol with trace CO	41
poly(acrylic acid methyl ester)	292–399	26% of products are volatile at 25° C, mainly methyl alcohol and CO ₂ with traces of monomer and methyl methacrylate and C ₄ - C ₆ oxygenated compounds, 74% of products are large chain fragments nonvolatile at 25° C	42, 43
poly(acrylic acid methyl ester)	up to 980	methanol (1.9%), methyl formate (trace), methyl acetate (1.4%), methyl acrylate (19.0%), methyl methacrylate (1.9%), saturated ester (2.1%), dimethyl glutarate (7.5%), methyl-4-methoxycarbonyl-pent-4-enoate (11.6%), trimethylpentane 1,3,5-tricarboxylate (0.6%), methyl 4,6-di-methoxycarbonylhept-6-enoate (53%), saturated and tetramers (1.0%)	44
poly(acrylic acid n-butyl ester)	300–500	major products CO ₂ , 1-butene, butanol, and chain fragments; minor products, butane, n-butyl acrylate, and n-butyl methacrylate	32
poly(acrylic acid n-propyl ester)	300–500	major products CO ₂ , propene, propanol, and chain fragments; minor products, propane, CO, H ₂ , n-propyl acrylate, and n-propyl methacrylate	32
poly(acrylic acid <i>tert</i> -butyl ester)	>160	86% isobutylene, 11% water, 3% CO ₂	45
poly(allyl cyanoacrylate)	350	better heat resistance than other cyanoacrylate for the crosslinked material; CO ₂ , chain fragments	
poly(ethyl cyanoacrylate)	320	cyanoacrylate monomer, CO ₂ ; the depolymerization process is intense above 260° C	

The results for a Py-GC/MS analysis of a sample of poly(methyl acrylate) (PMA) with $M_w = 30,000$ are shown in Figure 6.7.7. The pyrolysis was done at 600°C in He at a heating rate of 20°C/ms . The separation was done on a Carbowax column (60 m, 0.32 mm i.d. , $0.32\text{ }\mu\text{m}$ film thickness) with the GC starting at 40°C with a ramp of 2°C/min. up to 240°C and a final oven time of 20 min. (see Table 4.2.2). The MS was operated in EI+ mode. The peak identification for the chromatogram shown in Figure 6.7.7 was done using MS spectral library searches only and is given in Table 6.7.5.

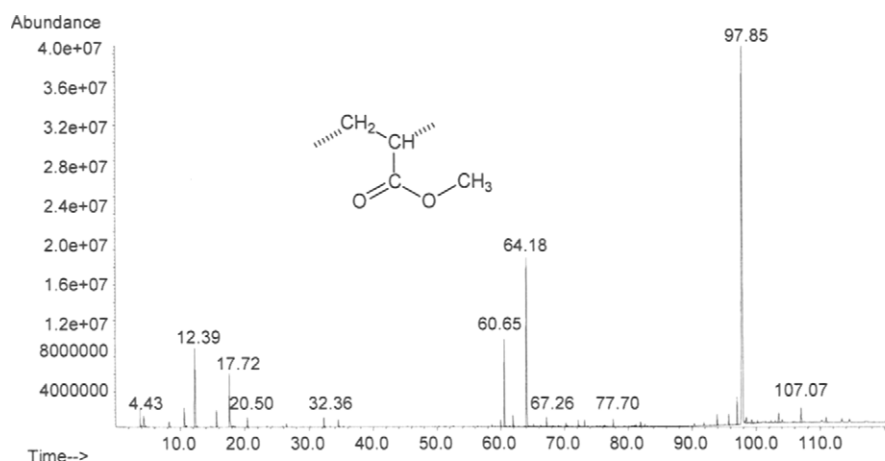
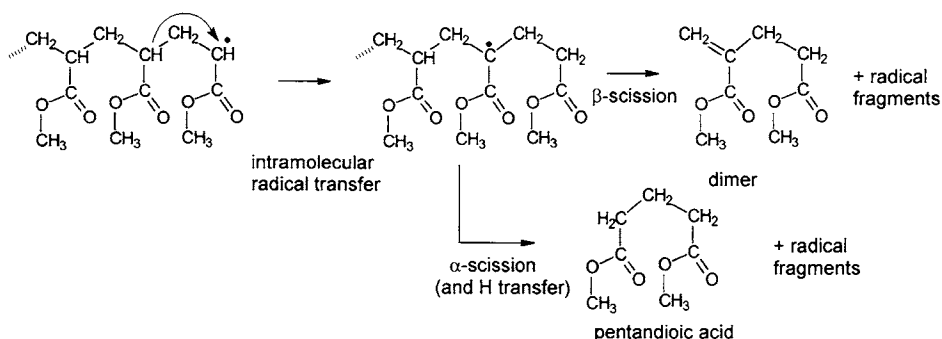


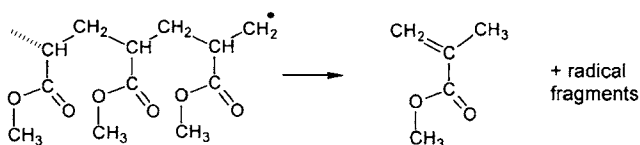
FIGURE 6.7.7. Result for a Py-GC/MS analysis of poly(methyl acrylate) $M_w = 30,000$. Pyrolysis done on 0.4 mg material at 600°C in He, with the separation on a Carbowax type column.

TABLE 6.7.5. Compounds identified in the pyrogram of poly(methyl acrylate) $M_w = 30,000$ shown in Figure 6.7.7.

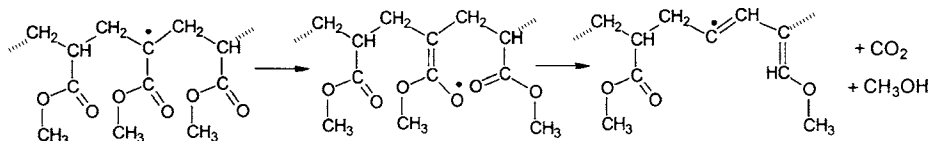
Peak	Compound	Ret. Time	MW	Area %
1	carbon dioxide	4.43	44	1.15
2	formaldehyde	5.08	30	trace
3	acetaldehyde	5.90	44	trace
4	acetic acid methyl ester	8.35	74	0.43
5	methanol	10.70	32	1.41
6	propanoic acid methyl ester	10.99	88	trace
7	2-propenoic acid methyl ester (monomer)	12.39	86	6.34
8	2-methyl-2-propenoic acid methyl ester	15.70	100	1.16
9	toluene	17.72	92	3.53
10	2-methylenebutanoic acid methyl ester	20.50	114	0.58
11	methylenecyclopropane carboxylic acid methyl ester	26.50	112	trace
12	styrene	32.36	104	0.59
13	ethoxyethyl acetate	34.62	132	0.45
14	benzaldehyde	50.28	106	trace
15	methylbutanedioic acid dimethyl ester	52.55	160	trace
16	4-methyl-2-pentendioic acid dimethyl ester	58.62	172	trace
17	2-methyl-pentanedioic acid dimethyl ester	60.05	174	0.41
18	pentanedioic acid dimethyl ester	60.65	160	5.88



The formation of 2-methyl-2-propenoic acid methyl ester from the second radical (2) is shown below:



Other reactions take place during pyrolysis. For example, some CO_2 is eliminated, probably in a reaction as follows:



The pyrolysis of poly(butyl acrylate) takes place similarly to the pyrolysis of poly(methyl acrylate). The results for a Py-GC/MS analysis of a 0.4 mg sample of poly(butyl acrylate) with $M_w = 60,000$ are shown in Figure 6.7.8. The pyrolysis and pyrolysate separation were done in the same conditions as those for other examples previously discussed (see Table 4.2.2). The MS was operated in EI+ mode and peak identification was obtained using MS spectral library searches only. The results are given in Table 6.7.6.

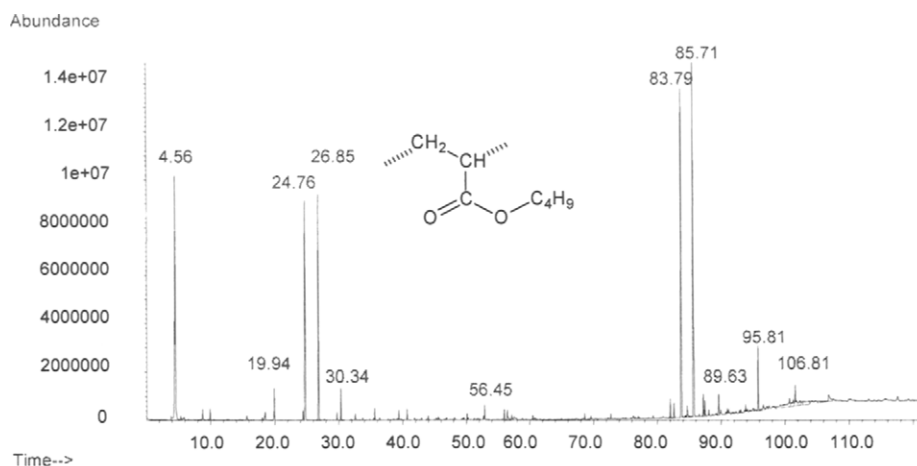


FIGURE 6.7.8. Result for a Py-GC/MS analysis of poly(butyl acrylate) $M_w = 60,000$. Pyrolysis done on 0.4 mg material at 600°C in He, with the separation on a Carbowax type column.

TABLE 6.7.6. Compounds identified in the pyrogram of poly(butyl acrylate) $M_w = 60,000$ shown in Figure 6.7.8.

Peak	Compound	Ret. Time	MW	Area %
1	carbon dioxide	4.41	44	4.25
2	1-butene	4.56	56	15.84
3	1,3-pentadiene	5.30	68	trace
4	butanal	9.96	72	0.51
5	4-ethenylcyclohexene	15.67	108	0.46
6	toluene	18.08	92	0.42
7	water	18.49	18	0.54
8	acetic acid butyl ester	19.94	116	1.35
9	propanoic acid butyl ester	24.41	130	0.55
10	1-butanol	24.76	74	14.60
11	2-propenoic acid butyl ester (monomer)	26.85	128	12.00
12	butanoic acid butyl ester	29.68	144	trace
13	2-methyl-2-propenoic acid butyl ester	30.34	142	1.37
14	styrene	32.74	104	trace
15	(E)-2-methyl-2-butenic acid butyl ester	35.63	156	0.55
16	(Z)-2-methyl-2-butenic acid butyl ester	39.53	156	0.53
17	2-hydroxy-propanoic acid butyl ester ?	50.35	146	trace
18	butyl (4E)-4-formylhex-4-enoate	52.82	198	0.53
19	butyl(2E,4E)-4-formylhexa-2,4-dienoate	55.98	196	0.49
20	butyl(2E,4Z)-4-formylhexa-2,4-dienoate	56.45	196	0.61
21	hexanedioic acid bis-butyl ester	82.05	258	0.88
22	pentanedioic acid bis-butyl ester	83.79	244	17.72
23	dibutyl 2-methylenepentane-1,5-dioate (dimer of butyl acrylate)	85.71	256	18.56
24	dibutyl(3E)-2-ethylidenepent-3-ene-1,5-dioate	87.22	268	1.16
25	unknown [(126(100), 182(81), 137(65), 81(52), 41(52), 86(49), 211(31)]	89.63		1.47
26	heptanedioic acid dibutylester	93.85	272	0.57
27	dibutyl 2-ethylidenepentane-1,5-dioate	95.81	270	3.03
28	dibutyl(2-(3-oxopropyl)hexane-1,6-dioate ?	106.81	314	2.02

Similar to the study of other pyrolysates, the analysis of the pyrolysate of poly(butyl acrylate) leads to some components that are difficult to identify. For example, the mass spectrum of dibutyl 2-methylenepentane-1,5-dioate (dimer of butyl acrylate) is not available in common mass spectral libraries, and it is shown in Figure 6.7.9.

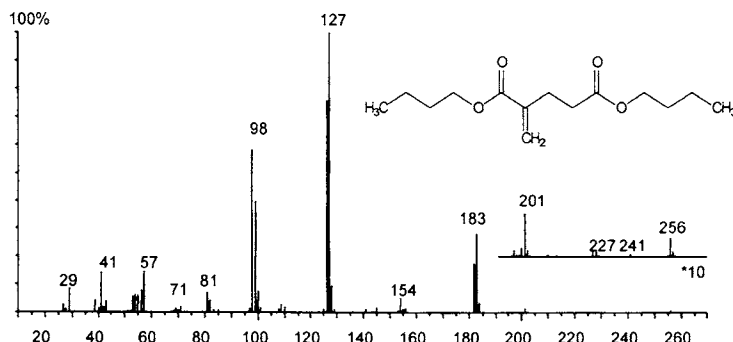
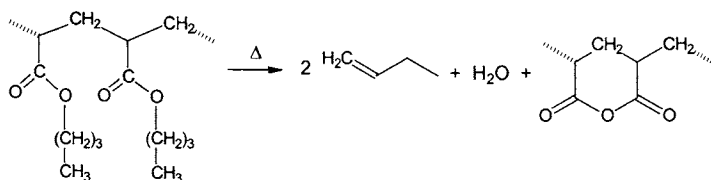
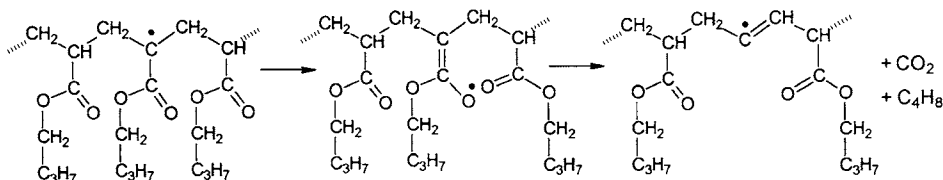


FIGURE 6.7.9. Mass spectrum of dibutyl 2-methylenepentane-1,5-dioate MW =256

A higher level of monomer, butanol, and pentanedioic acid bis-butyl ester appear to be formed from the pyrolysis of poly(butyl acrylate) as compared to that of PMA. However, this can be just an artifact of the calculation based on the data from the pyrogram. A trimer of butyl acrylate cannot be seen in the conditions used to generate the pyrogram from Figure 6.7.8 because of its higher MW. This compound does not elute from the chromatographic column even if present in the pyrolysate. For this reason, its formation cannot be confirmed. Other compounds with high polarity also may be retained in the chromatographic column. For example, derivatives of 3H-4,5-dihydropyran-dione were not detected in the pyrogram, and their presence cannot be confirmed or disproved. However, the presence of 1-butene and that of water in the pyrolysate indicate that the reaction shown below is common during pyrolysis:



The formation of some CO₂ and of butene can be explained by reactions as shown below:



Similar to the results for pyrolysis of PMA and poly(butyl acrylate) are those for the pyrolysis of poly(2-ethylhexyl acrylate). The Py-GC/MS analysis of a sample of poly(2-ethylhexyl acrylate) is shown in Figure 6.7.10. The experimental conditions were similar to those for poly(butyl acrylate), namely 600° C in He at a heating rate of 20° C/ms with the separation on a Carbowax column (see Table 4.2.2). The peak identification for the chromatogram shown in Figure 6.7.10 was done using MS spectral library searches only and is given in Table 6.7.7.

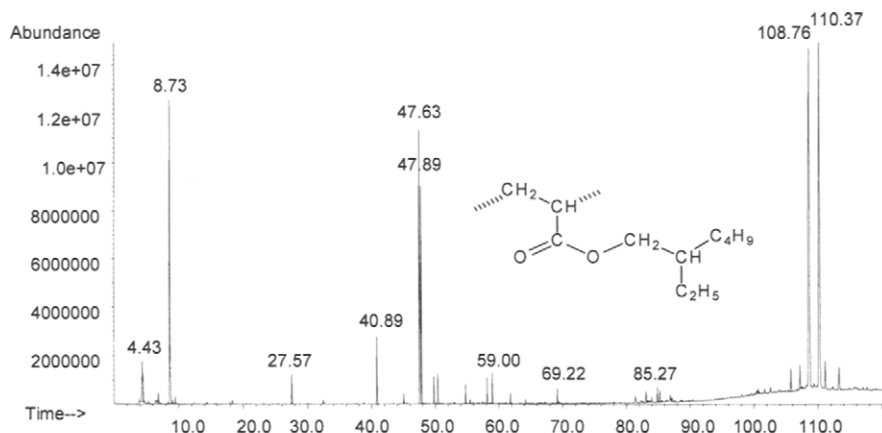


FIGURE 6.7.10. Result for a Py-GC/MS analysis of poly(2-ethylhexyl acrylate) $M_w = 92,000$. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 6.7.7. Compounds identified in the pyrogram of poly(2-ethylhexyl acrylate) $M_w = 92,000$ shown in Figure 6.7.10 and obtained at 600° C.

Peak	Compound	Ret. Time	MW	Area %
1	carbon dioxide	4.44	44	1.81
2	1-butene	4.55	56	0.92
3	2-heptene	6.80	98	trace
4	1,3-hexadiene	6.89	82	trace
5	3-methylheptane	6.93	114	0.46
6	3-methylene-heptane	8.73	112	13.97
7	3-methyl-1-heptene	9.10	112	trace
8	3-methyl-2-heptene	9.53	112	trace
9	1,2-dimethyl-cyclohexene	14.40	110	trace
10	toluene	17.95	92	trace
11	water	18.32	18	trace
12	hexanal	20.50	100	trace
13	2-ethylhexanal	27.57	128	0.92
14	styrene	32.47	104	trace
15	acetic acid 2-ethylhexyl ester	40.89	172	2.03
16	2-propenoic acid 2-ethylhexyl ester (monomer)	47.63	184	13.49
17	2-ethylhexanol	47.89	130	8.60
18	isobutanoic acid 2-ethylhexyl ester	49.81	200	0.80

TABLE 6.7.7 (continued). Compounds identified in the pyrogram of poly(2-ethylhexyl acrylate) $M_w = 92,000$ shown in Figure 6.7.10 and obtained at 600° C.

Peak	Compound	Ret. Time	MW	Area %
19	2-propenoic acid 3-methylheptyl ester ?	50.41	184	0.89
20	2-methyl-2-propenoic acid 2-ethylhexyl ester	54.80	198	0.59
21	2-methyl-2-butanoic acid 2-ethylhexyl ester	58.19	214	0.78
22	2-methyl-2-butenoic acid 2-ethylhexyl ester	59.00	212	0.91
23	unknown [83(100), 70(45), 55(30), 84(30), 112(17)]	61.83		0.31
24	cyclohexanecarboxylic acid methyl ester ?	69.22	142	0.43
25	3-pentylpentanedioic acid ?	83.13	202	0.36
26	unknown [57(100), 70(96), 71(94), 114(88), 55(68)...184(9)]	84.91	226	0.52
27	unknown [140(100), 57(62), 71(49), 126(42), 196(25)]	85.27		0.45
28	di-(2-ethylhexyl) 2-methylpentane-1,5-dioate	105.79	370	1.00
29	1,2-cyclohexanedicarboxylic acid bis(2-ethylhexyl) ester	107.23	378	0.95
30	pentanedioic acid bis-(2-ethylhexyl) ester	108.76	356	22.43
31	bis-(2-ethylhexyl)-2-methylenepentane-1,5-dioate (dimer of 2-ethylhexyl acrylate)	110.37	368	24.78
32	4-methyl-cyclohexane-1,2-dicarboxylic acid bis(2-ethylhexyl) ester	111.18	392	1.30
33	4-methyl-cyclohexene-1,2-dicarboxylic acid bis(2-ethylhexyl) ester	113.34	390	1.28

Some of the mass spectra for the peaks eluting at higher retention times are not available in common mass spectral libraries. This is the case, for example, for pentanedioic acid bis-(2-ethylhexyl) ester, with the mass spectrum shown in Figure 6.7.11, and for bis-(2-ethylhexyl)-2-methylenepentane-1,5-dioate (dimer of 2-ethylhexyl acrylate), with the mass spectrum shown in Figure 6.7.12.

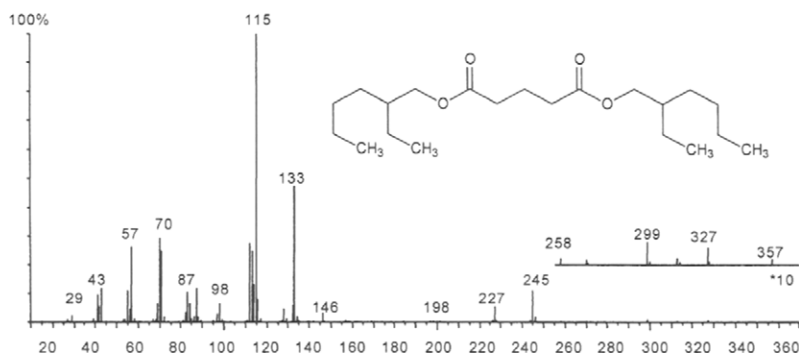


FIGURE 6.7.11. Mass spectrum of pentanedioic acid bis-(2-ethylhexyl) ester MW = 356.

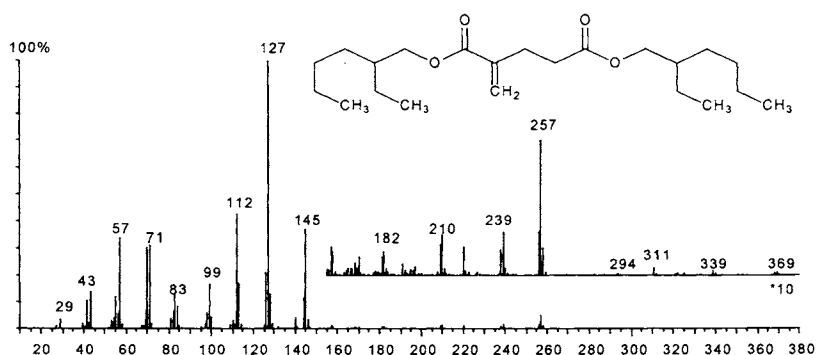


FIGURE 6.7.12. Mass spectrum of bis-(2-ethylhexyl)-2-methylenepentane-1,5-dioate MW =368.

As seen from several examples, the main characteristic of pyrolysis of poly(acrylic acid esters) is the formation of monomer, dimer, trimer, etc. The specific yield of monomer, dimer, trimer, etc. is temperature dependent, higher temperatures favoring the formation of lower molecular weight compounds.

- Copolymers of acrylic acid and of its esters

Acrylic acid can be used as comonomer in different copolymers. The most common of these are probably poly(ethylene-co-acrylic acid) (see Section 6.1, Figure 6.1.7), poly(acrylic acid-co-acrylamide), and poly(acrylic acid-co-styrene-co-acrylonitrile) or ASA terpolymer. The acrylic acid in the poly(ethylene-co-acrylic acid) increases the wettability of the polymer. Different salts of poly(acrylic acid-co-acrylamide) are used in the water purification processes as water clarification aid and in drilling fluids. Additional -COOH groups make the polymer even more hydrophilic, and polymers such as poly(acrylic acid-co-maleic acid) are easily water soluble and used as liquid thickeners. In ASA terpolymer acrylic acid brings more flexibility and the material has very good mechanical properties and weather resistance. For these reasons ASA is extensively used in automotive industry and in the fabrication of various appliances. Even more frequently than acrylic acid itself, various acrylates are used in copolymers. Among these can be mentioned the copolymers of acrylic acid esters with methacrylic acid esters such as poly(methyl methacrylate-co-methyl acrylate), poly(methyl methacrylate-co-ethyl acrylate), poly(methyl methacrylate-co-butyl acrylate), poly(ethyl methacrylate-co-ethyl acrylate), poly(acrylonitrile-co-methyl acrylate), poly(alkyl acrylate-co-methyl methacrylates), and poly(alkyl acrylate-co-hydroxyethyl methacrylates) where alkyl can be methyl, ethyl, butyl, etc. Some literature information regarding thermal decomposition of copolymers including acrylic acid and acrylic acid esters is given in Table 6.7.8 [6].

TABLE 6.7.8. Summary regarding literature information on thermal decomposition of copolymers including acrylic acid and acrylic acid esters.

Polymer	Temp. °C	Results	Ref.
poly(ethyl acrylate-co-butyl methacrylate)	500	monomers, dimers, peak intensities used for the analysis of copolymer composition	46
poly(ethyl acrylate-co-styrene-co-ethyl methacrylate)	500	monomers, dimers, peak intensities used for the analysis of copolymer composition	46
poly(methyl acrylate)-blend-poly(2-bromoethyl methacrylate) 50/50 w/w	ambient to 500	CO ₂ , ketene (minor), methyl bromide, vinyl bromide (minor), acetaldehyde, methanol, methyl methacrylate, methyl acrylate, 1,2-dibromoethane, 2-bromoethyl methacrylate	47
poly(<i>tert</i> -butyl acrylate-co-glycidyl methacrylate) 34/66	0–700	CO, CO ₂ , propene, ethanal, isobutene, acrolein, allyl alcohol	48
various acrylic acid copolymers		comonomer identification in the polymer	49
poly(methyl acrylate-co-bromoethyl methacrylate) 10–82 mol% MA	ambient to 500	CO ₂ , ketene, methyl bromide, acetaldehyde, methyl acrylate, methanol, 1,2-dibromoethane, methyl methacrylate, 2-bromoethanol ethyl methacrylate, CH ₄ , CO, H ₂ modified chain fragments	50
poly(<i>n</i> -butyl acrylate-co-methyl methacrylate) 3.9–93.4 mol% BA	313–332	1-butene, CO ₂ , butanol, methyl methacrylate, butyl acrylate, butyl methacrylate; small quantities of methane, ethane, propane, butane, ethylene, propene, <i>cis</i> -, and <i>trans</i> -2-butene, H ₂ , and CO that increase with butyl acrylate content of the copolymer	51
poly(methyl acrylate-co-methyl methacrylate) mole ratios 112/1–2/1	ambient to 500	monomers, CO ₂ , chain fragments larger than monomer, H ₂ , more stable than poly(methyl methacrylate); rapid decrease in molecular weight; products of photodegradation at 170° by 254 nm radiation are qualitatively similar	52, 53
poly(acrylonitrile-co-methyl acrylate) 1:1 copolymer	360–500	51% weight loss	54
poly(methyl acrylate-co-acryloyl chloride) 6, 15, 41, 83 mol% AC	ambient to 500	acrylic acid, HCl, H ₂ O, CO, CO ₂ , acryloyl chloride, methyl acrylate, 262 methyl acrylate chain fragments, anhydride and γ -lactone structures, chloromethane, methyl methacrylate, methanol, 3,5-(6-chloro-2-pyrone) and fragments thereof, C ₆ , C ₉ , C ₁₂ , C ₁₅ fragments. Relative yields depend upon copolymer composition	55

Several studies regarding the use of pyrolysis for the analysis of acrylic acid and acrylate copolymers were reported in literature [56–59], etc. One such study used pyrolysis in the presence of tetramethylammonium hydroxide (TMAH) for the analysis of several UV-cured acrylic ester resins [60]. The materials evaluated included the UV-cured resins formed from ethylene oxide and bisphenol A diacrylate (EBADA), and copolymers of acrylated polyfunctional aliphatic alcohols (such as pentaerythritol triacrylate) and dipentaerythritol hexacrylate (DPEHA). The compositions of the UV-cured resins containing multi-component acrylic esters were analyzed based on the relative yields of the characteristic pyrolysates of each acrylic ester. The EBADA resin pyrolysate contained methyl acrylate (MA) and various dimethyl ethers of ethylene oxide modified bisphenol A, reflecting the numbers of ethylene oxide units in the original EBADA. The pyrograms of the UV-cured resins of acrylated polyfunctional aliphatic alcohols contained methyl ethers reflecting the structure of the original alcohols. Considerable amounts of pyrolysates with non-methylated hydroxyl groups also were

detected for aliphatic alcohol moieties. For calibration purposes, a series of UV-cured standard samples, which contained known amounts of the individual acrylic ester and neopentylglycol diacrylate (NPGDA) were used as internal standards. The compositions of the multi-component UV-cured resins determined using this approach showed good agreement with the theoretical values estimated from the feed composition.

The results for a Py-GC/MS analysis of a poly(acrylic acid-co-maleic acid) sample are shown in Figure 6.7.13. The polymer has $M_w = 3,000$, CAS# 29132-58-9, and the idealized formula $[-CH_2-CH(COOH)-]_x[-CH(COOH)-CH(COOH)-]_y$. The pyrolysis was done at 600°C in He at a heating rate of 20°C/msec with 10 sec. THT. The separation was done on a Carbowax column (60 m, 0.32 mm i.d., 0.32 μm film thickness) with the GC starting at 40°C with a ramp of 2°C/min. up to 240°C and a final oven time of 20 min. (see Table 4.2.2). The MS was operated in EI+ mode. The peak identification for the chromatogram shown in Figure 6.7.13 was done using MS spectral library searches and is given in Table 6.7.9.

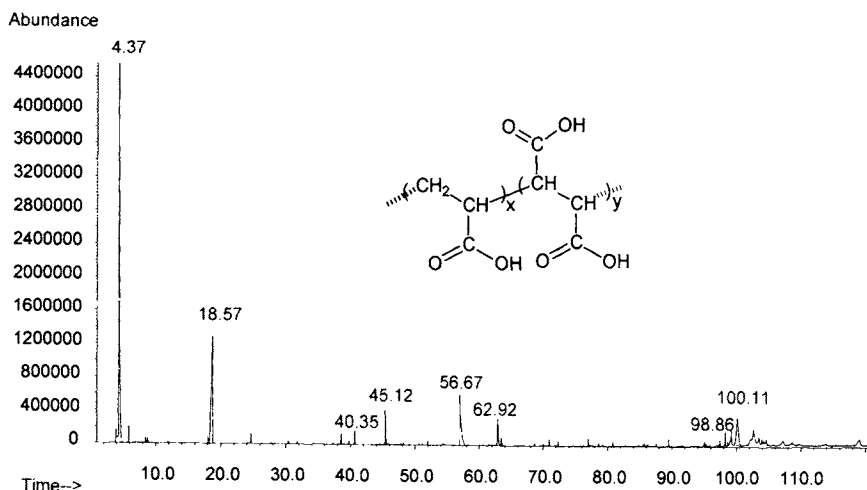


FIGURE 6.7.13. Result for a Py-GC/MS analysis of poly(acrylic acid-co-maleic acid) $M_w = 3,000$. Pyrolysis done on 0.4 mg material at 600°C in He, with the separation on a Carbowax type column.

As seen in Table 6.7.9 some of the fragment molecules in the pyrolysate of poly(acrylic acid-co-maleic acid) are similar to those of the pyrolysate of poly(acrylic acid). A large proportion of CO_2 resulting from the decarboxylation reactions and of water is seen, as expected, in the pyrolysate. Some 2-propenoic acid at levels higher than from the homopolymer also is generated, indicating that some unzipping of the polyacrylic acid sequences may take place. Among the compounds formed for the maleic acid moiety are 3,4-dimethyl-2,5-furandione and 3-methyl-4-ethyl-2,5-furandione. These are the result of reactions of water elimination between two carboxyl groups and backbone cleavage.

TABLE 6.7.9. Compounds identified in the of poly(acrylic acid-co-maleic acid) $M_w = 3,000$ as shown in Figure 6.7.13.

Peak	Compound	Ret. time	MW	Area %
1	carbon dioxide	4.37	44	59.81
2	toluene	17.89	92	trace
3	water	18.57	18	19.09
4	1,2-dimethylbenzene	24.40	106	trace
5	cyclopentanone	27.79	84	trace
6	1-ethyl-3-methylbenzene	30.20	120	trace
7	3-methylcyclohex-3-en-1-one	38.27	110	trace
8	2-methyl-2-cyclopenten-1-one	40.35	96	trace
9	acetic acid	45.12	60	2.48
10	2-propenoic acid	56.67	72	8.51
11	3,4-dimethyl-2,5-furandione	62.92	126	2.63
12	3-methyl-4-ethyl-2,5-furandione	63.46	140	trace
13	2,3-dimethyl-4-hydroxy-2-butenic acid lactone	71.14	112	trace
14	2,6-dimethylphenol	72.03	122	trace
15	2-methylphenol	76.72	108	trace
16	3-ethyl-2H-1-benzopyran-2-one	97.91	174	trace
17	3-methyl-2H-1-benzopyran-2-one	98.86	160	trace
18	unknown	100.11		7.48

Another Py-GC/MS experiment was performed on polyacrylic-*inter-net*-polysiloxane, a copolymer used as impact properties modifier. This is a polymer of butyl acrylate with low levels of allyl, methyl, and 3-(dimethoxymethylsilyl)propyl methacrylates interpenetrated with cyclic dimethylsiloxane. The copolymer has CAS # 143106-82-5. The pyrolysis was done at 600° C in He similar to other experiments previously discussed. The pyrogram is shown in Figure 6.7.14 and peak identification is given in Table 6.7.10.

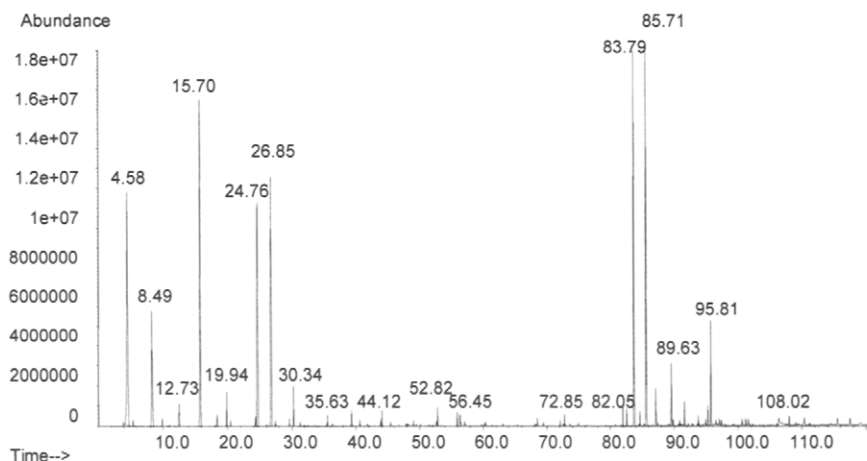
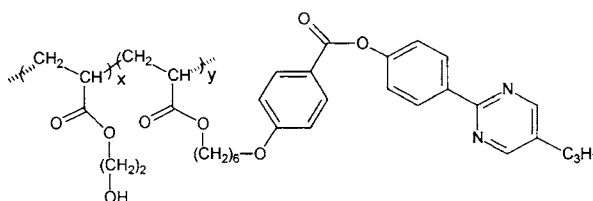


FIGURE 6.7.14. Result for a Py-GC/MS analysis of a copolymer of butyl acrylate with low levels of allyl, methyl, and 3-(dimethoxymethylsilyl)propyl methacrylates interpenetrated with cyclic dimethylsiloxane. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 6.7.10. Compounds identified in the a copolymer of butyl acrylate with low levels of allyl, methyl, and 3-(dimethoxymethylsilyl)propyl methacrylates interpenetrated with cyclic dimethylsiloxane as shown in Figure 6.7.14.

Peak	Compound	Ret. time	MW	Area%
1	carbon dioxide	4.41	44	3.59
2	1-butene	4.56	56	10.95
3	hexamethylcyclotrisiloxane	8.49	222	4.74
4	octamethylcyclotetrasiloxane	12.73	296	0.73
5	2-methyl-2-propenoic acid methyl ester	15.70	100	15.30
6	water	18.46	18	0.46
7	acetic acid butyl ester	19.94	116	0.85
8	decamethylcyclopentasiloxane	20.88	370	trace
9	propanoic acid butyl ester	24.41	130	0.24
10	1-butanol	24.76	74	11.05
11	2-propenoic acid butyl ester (monomer)	26.85	128	10.10
12	2-methyl-2-propenoic acid butyl ester	30.34	142	0.98
13	dodecamethylcyclohexasiloxane	31.74	444	trace
14	(E)-2-methyl-2-butenic acid butyl ester	35.63	156	0.25
15	(Z)-2-methyl-2-butenic acid butyl ester	39.53	156	0.39
16	tetradecamethylcycloheptasiloxane	42.25	518	trace
17	dimethylbutoxysilanol ?	44.12	148	0.35
18	butyl (4E)-4-formylhex-4-enoate	52.82	198	0.45
19	butyl(2E,4E)-4-formylhexa-2,4-dienoate	55.98	196	0.39
20	butyl(2E,4Z)-4-formylhexa-2,4-dienoate	56.45	196	0.39
21	unknown [112(100), 126(54), 95(51), 141(47), ..196(9)]	72.85		0.27
22	hexanedioic acid bis-butyl ester	82.05	258	0.54
23	2-methylenehexanedioic acid bis-butyl ester	82.59	270	0.48
24	pentanedioic acid bis-butyl ester	83.79	244	15.64
25	?-methyl-2-methylenehexanedioic acid bis-butyl ester	84.68	284	0.40
26	dibutyl 2-methylenepentane-1,5-dioate (dimer of butyl acrylate)	85.71	256	14.00
27	dibutyl(3E)-2-ethylidenpent-3-ene-1,5-dioate	87.22	268	1.09
28	unknown [(126(100), 182(81), 137(65), 81(52), 41(52), 86(49), 211(31)]	89.63		2.07
29	unknown [151(100), 95(87), 224(75), 150(74), 196(52), 123(51), 140(48)]	91.64		0.65
30	heptanedioic acid dibutylester	93.85	272	0.26
31	dibutyl 2-ethylidenepentane-1,5-dioate	95.81	270	3.03
32	unknown	108.02		0.36

The pyrolysate of polyacrylic-*inter-net*-polysiloxane copolymer contains as main fragment molecules pyrolysis products similar to those of poly(butyl acrylate) and of poly(dimethylsiloxane (see Figure 6.7.8. and Section 16.1). The identification of fragments that would indicate sequences of other comonomers or any molecular connections between the two types of comonomer units was not possible. Other copolymers with acrylic acid as comonomer were studied using analytical pyrolysis. Among these are copolymers with special properties such as the copolymer with the formula shown below:



This copolymer forms liquid crystalline phases and self organize in thin films. The pyrolysis using continuous heating from 50 to 700° C generates initially phenol derivatives, then compounds resulting from the acrylic sequence, and further other fragments from the two comonomer units [61].

The pyrograms for poly(acrylamide-co-acrylic acid) 1.5 wt % acrylic acid, CAS# 9003-06-9, and for poly(acrylic acid-co-acrylamide) potassium salt, CAS# 90363-65-8, are given in Figure 6.7.22 and 6.7.23 respectively. Since the level of acrylic acid in these copolymers is low, the pyrograms are dominated by the pyrolysis products of polyacrylamide (see Figure 6.7.15).

- **Polyacrylamide and substituted polyacrylamides**

Other derivatives of acrylic acid, such as acrylamide, and some substituted acrylamides also are utilized to make polymers with practical applications. For example, polyacrylamide that is water soluble is used in medicine, in paints and coatings industry, and in adhesives industry. The polymer with some crosslinking forms hydrogels, with applications in agriculture (soil improvement, hydroponics) and in laboratories as stationary phase for electrophoresis.

Polyacrylamide, CAS# 9003-06-9, can be obtained by free radical polymerization of acrylamide using an initiator, such as persulfate [62–65]. The properties of the gels are highly influenced by their degree of crosslinking, which is typically achieved using N,N'-methylenebisacrylamide. Various reports on polyacrylamide pyrolysis are given in literature [66, 67]. A pyrogram of a polyacrylamide sample with $M_w = 10,000$ is shown in Figure 6.7.15. The conditions for pyrolysis and for the analysis of pyrolysate are the same as those used for the analysis of other example polymers previously discussed (see Table 4.2.2). The peak identification in the pyrogram was done using MS library searches only and is given in Table 6.7.11.

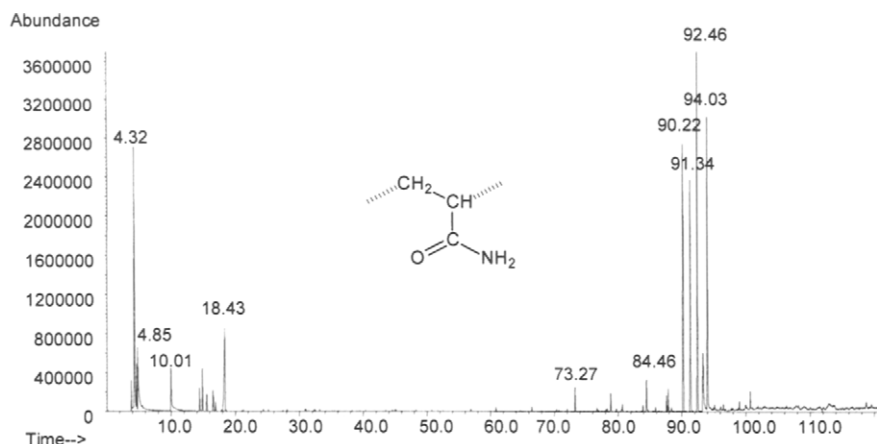


FIGURE 6.7.15. Result for a Py-GC/MS analysis of polyacrylamide $M_w = 10,000$. Pyrolysis done on 0.4 mg material at 600°C in He, with the separation on a Carbowax type column.

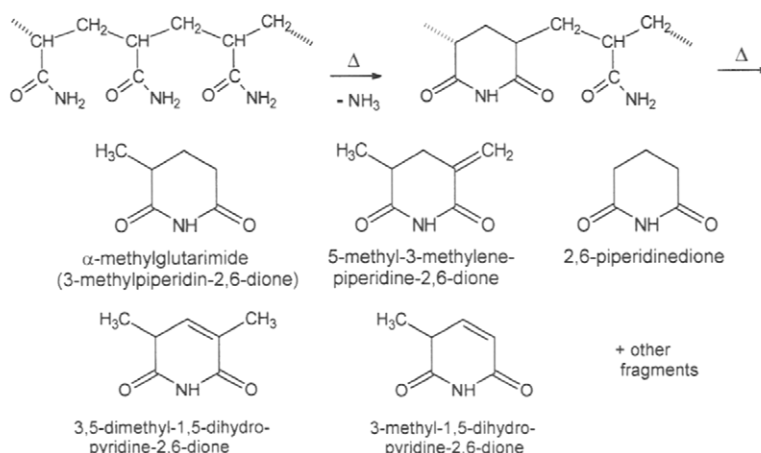
TABLE 6.7.11. Compounds identified in the pyrogram of polyacrylamide $M_w = 10,000$ shown in Figure 6.7.15 and obtained at 600°C .

Peak	Compound	Ret. Time	MW	Area %
1	carbon dioxide	4.32	44	11.96
2	ammonia	4.85	17	4.66
3	sulfur dioxide (impurity)	10.01	64	3.09
4	2-methyl-2-propenenitrile	14.48	67	0.92
5	acrylonitrile (2-propenenitrile)	15.09	53	1.78
6	acetonitrile	15.79	41	trace
7	hydrogen cyanide	16.57	27	trace
8	propanenitrile (propionitrile)	16.89	55	trace
9	water	18.43	18	7.78
10	1,2-dimethylbenzene	24.40	106	trace
11	1,4-dimethylbenzene	27.38	106	trace
12	styrene	32.51	104	trace
13	2-methylcyclohexanone	36.08	112	trace
14	2-methyl-2-cyclopenten-1-one	40.35	96	trace
15	3-methyl-2-cyclohexen-1-one	44.98	110	trace
16	acetic acid	45.12	60	trace
17	indene	47.90	116	trace
18	propanoic acid	50.67	74	trace
19	2-propenoic acid	56.67	72	trace
20	2-methyl-2-propenoic acid	59.87	86	trace
21	2-methylenebutanoic acid	66.61	100	trace
22	1-methylnaphthalene	69.70	142	trace
23	2,6-dimethylphenol	72.03	122	trace
24	2-propenamide (acrylamide)	73.27	71	1.07
25	2-methylphenol ?	76.68	108	trace
26	1-buten-2,4-dicarbonitrile	79.41	106	trace

TABLE 6.7.11 (continued). Compounds identified in the pyrogram of polyacrylamide $M_w = 10,000$ shown in Figure 6.7.15 and obtained at 600° C.

Peak	Compound	Ret. Time	MW	Area %
27	unknown [55(100), 123(41), 42(32), 67(18), 27(6)]	84.46	123	1.58
28	unknown [56(100), 99(34), 141(30), 113(14), 70(13)]	87.88	141	0.99
28	3-methylpiperidin-2,6-dione (α -methylglutarimide)	90.22	127	13.58
30	3,5-dimethyl-1,5-dihydropyridine-2,6-dione ?	91.34	139	11.44
31	2,6-piperidinedione	92.46	113	20.98
32	5-methyl-3-methylenepiperidine-2,6-dione ?	93.31	139	4.28
33	3-methylenepiperidine-2,6-dione ?	94.03	125	15.90

The main peaks in the pyrogram of polyacrylamide are several piperidinediones such as 3-methylpiperidin-2,6-dione (α -methylglutarimide), 3,5-dimethyl-1,5-dihydropyridine-2,6-dione, 2,6-piperidinedione, 5-methyl-3-methylenepiperidine-2,6-dione, and 3-methylenepiperidine-2,6-dione. These molecules and the presence of ammonia in the pyrolysate show that very likely the main reaction during pyrolysis is an elimination that takes place with the formation of piperidin-2,6-dione cycles followed by further cleavages and formation of small molecules as shown below:



The identification of these compounds in the pyrolysate is based on the tentative identifications using the mass spectra of several peaks from the pyrogram shown in Figure 6.7.15. Two spectra for the peaks eluting at 91.34 min. and 93.31 min. showing the molecular ion $m/z = 139$ indicate the presence of two related compounds, 3,5-dimethyl-1,5-dihydro-pyridine-2,6-dione (MW = 139) and 5-methyl-3-methylenepiperidine-2,6-dione. However, the spectra are not retrievable from common mass spectral libraries, and it cannot be unambiguously determined which spectrum belongs to which compound. The two spectra are shown in Figure 6.7.16.

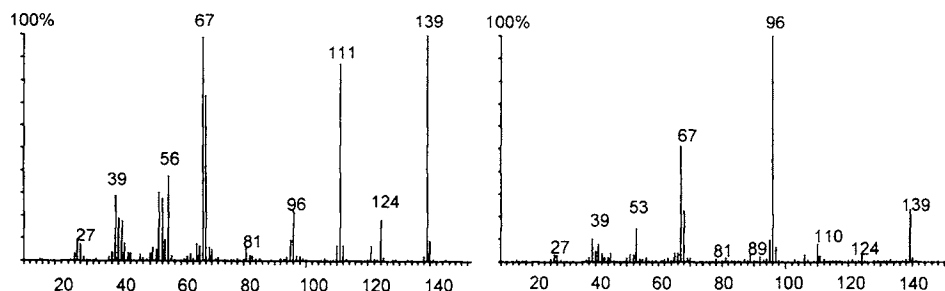
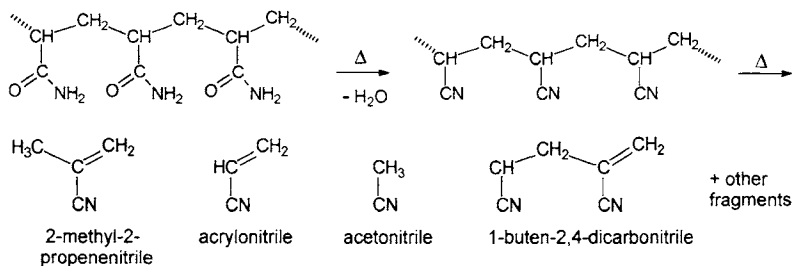


FIGURE 6.7.16. Mass spectra of two peaks in the pyrogram of polyacrylamide (eluting at 91.34 min. and 93.31 min.) indicating the presence of 3,5-dimethyl-1,5-dihydropyridine-2,6-dione and of 5-methyl-3-methylenepiperidine-2,6-dione, both with MW = 139.

The peak eluting in the pyrogram of polyacrylamide at 94.03 min. belongs either to 3-methylene-piperidine-2,6-dione or to 3-methyl-1,5-dihydropyridine-2,6-dione (MW = 125). Some of the compounds generated from polyacrylamide pyrolysis are potentially toxic [e.g., LD50 oral (rat) for 2,6-piperidinedione is 2 mg/Kg].

As seen from the list of compounds present in polyacrylamide pyrolysate, it also contains some water ($\approx 8\%$). The water can be eliminated from the amide groups attached to the polymer backbone, generating a polymeric nitrile, which further decomposes as shown below:



A small level of monomer in the pyrolysate (about 1%) indicates that some cleavage of the polymer backbone takes place without dehydration of the amide group. Therefore, some water may be formed by elimination from the small molecules containing amido groups, further leading to the same compounds as those generated by the cleavage of the nitrile type polymer.

Besides water, another small molecule in the pyrolysate is CO_2 . This small molecule may be eliminated by various mechanisms including a hydrolysis of the amide groups with the formation of acrylic acid, followed by decarboxylation. Some small peaks in the pyrolysis of polyacrylamide are identical with those from poly(acrylic acid). Even traces of propanoic acid and propenoic acid are present in the acrylamide pyrolysate. A comparison between a time window 25.0 min. to 70 min. from the pyrogram of poly(acrylic acid) and from the pyrogram of polyacrylamide is shown in Figure 6.7.17.

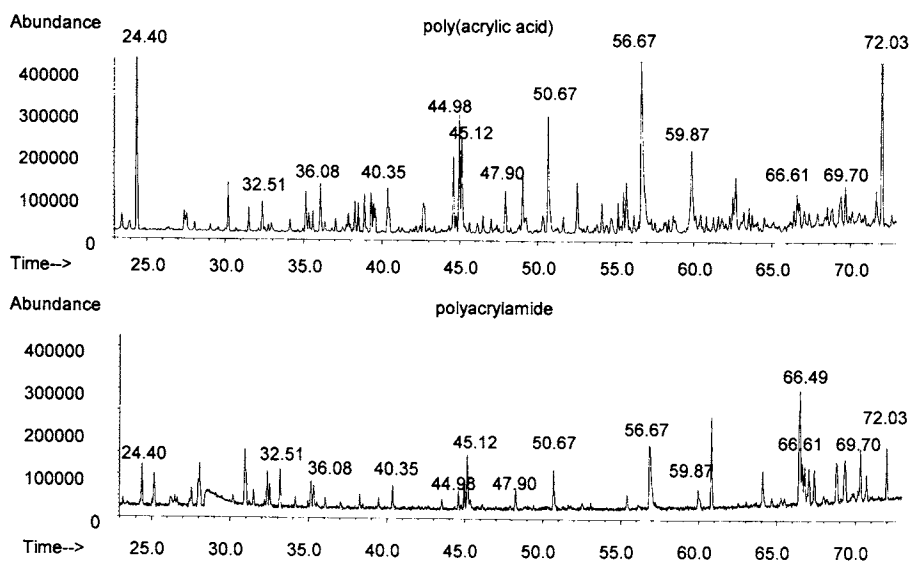


FIGURE 6.7.17. Comparison between a time window 25.0 min to 70 min. from the pyrogram of poly(acrylic acid)(see Figure 6.7.2) and from the pyrogram of polyacrylamide (see Figure 6.7.15).

The peaks shown in Figure 6.7.17 correspond to trace components in the pyrolysate. Their intensities are usually different in the two pyrograms, indicating different levels of compound. However, the identity of some of the components can be verified from identical retention times and mass spectra.

Pyrolysis results for poly(N-isopropylacrylamide), CAS# 25189-55-3, with the idealized formula $\{-\text{CH}_2\text{-CH}[\text{CONH}(\text{i-C}_3\text{H}_7)]-\}_n$ are very similar to that of poly(acrylamide). The reaction of elimination of 2-propanamine that was detected in the pyrolysate is similar to the elimination of ammonia from polyacrylamide. A pyrogram of a poly(N-isopropylacrylamide) sample with $M_w = 20,000\text{--}25,000$ is shown in Figure 6.7.18. The conditions for pyrolysis and for the analysis of pyrolysate were the same as those used for the analysis of other example polymers previously discussed (see Table 4.2.2). The peak identification in the pyrogram was done using MS library searches and is given in Table 6.7.12.

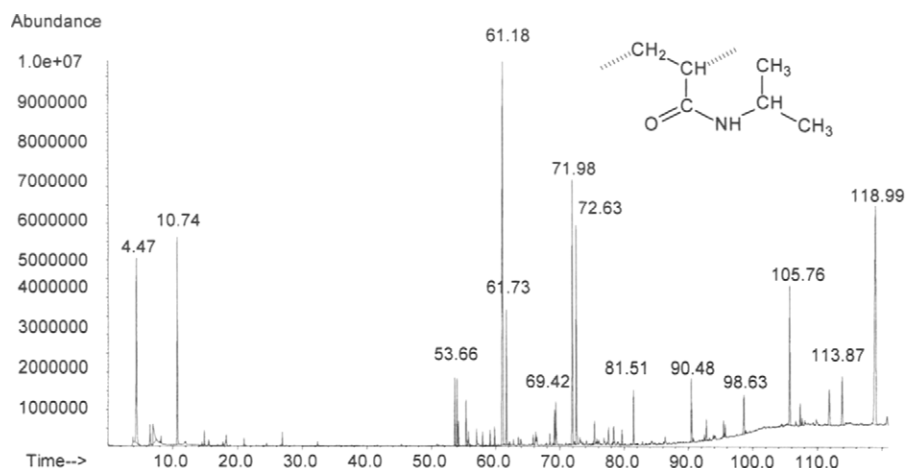


FIGURE 6.7.18. Result for a Py-GC/MS analysis of poly(*N*-isopropylacrylamide) $M_w = 20,000$ – $25,000$. Pyrolysis done on 0.4 mg material at 600°C in He, with the separation on a Carbowax type column.

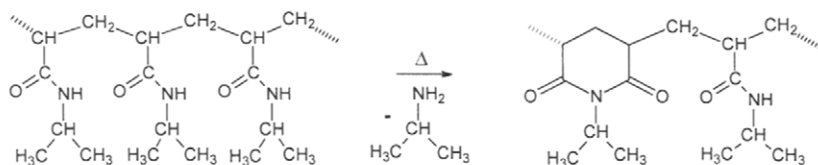
TABLE 6.7.12. Compounds identified in the pyrogram of poly(*N*-isopropylacrylamide) $M_w = 20,000$ – $25,000$ shown in Figure 6.7.18 and obtained at 600°C .

Peak	Compound	Ret. Time	MW	Area %
1	1-propene	4.47	42	8.44
2	propan-2-isocyanate	6.57	85	0.74
3	2-propanamine	7.04	59	1.36
4	N-(1-methylethylidene)-2-propanamine	10.74	99	7.40
5	2-propenenitrile	14.91	53	trace
6	2-methylpropanenitrile	15.51	69	trace
7	water	18.25	18	trace
8	3-methyl-2-methylenebutanenitrile	21.00	95	trace
9	1-butanol	24.48	74	trace
10	3-(2-propenyl)-1-cyclopentene	26.92	108	trace
11	styrene	32.35	104	trace
12	acetic acid	45.28	60	trace
13	N-isopropylacetamide	53.66	101	1.99
14	N-(methylethyl)but-3-enamide	54.05	127	1.78
15	N-(methylethyl)propanamide	54.22	115	0.64
16	N-isopropylformamide	55.43	87	1.40
17	3,4-diethyl-1H-pyrole-2,5-dione	55.76	153	0.45
18	2-methyl-N-(methylethyl)-3-butenamide	57.06	141	0.45
19	N-(methylethyl)butanamide	57.98	129	0.45
20	3,4-dimethyl-N-(methylethyl)-1H-pyrole-2,5-dione	59.15	167	0.45
21	N-(methylethyl)pent-3-enamide	59.84	141	0.56
22	N-(1-methylethyl)-2-propenamide (monomer)	61.18	113	21.08
23	2-methylene-N-(1-methylethyl)hexanamide	61.73	169	3.81
24	3-methyl-1-(methylethyl)piperidine-2,6-dione	69.19	169	1.08
25	5-methyl-3-methylene-1-(methylethyl)piperidine-2,6-dione	69.42	181	1.42
26	1-(methylethyl)piperidine-2,6-dione	71.98	155	8.70
27	3-methylene-1-(methylethyl)piperidine-2,6-dione	72.63	167	6.77

TABLE 6.7.12 (continued). Compounds identified in the pyrogram of poly(*N*-isopropylacrylamide) $M_w = 20,000$ – $25,000$ shown in Figure 6.7.18 and obtained at 600°C .

Peak	Compound	Ret. Time	MW	Area %
28	3,5-dimethylene-1-(methylethyl)piperidine-2,6-dione ?	75.41	179	0.83
29	1,3,5-1H-pyrazole ?	81.51	110	1.67
30	unknown [165(100), 207(91), 164(75), 150(44), 77(16)]	90.48		1.97
31	unknown [44(100), 41(26), 139(20), 154(16), 96(16)]	98.63		1.39
32	N-(methylethyl)-N'-(methylethyl)pent-2-ene-1,5-diamide ?	105.76	212	5.36
33	N-(methylethyl)-N'-(methylethyl)-2-vinylpentane-1,5-diamide ?	107.38	240	0.83
34	unknown [142(100), 100(95), 58(37), 126(36), 114(33),...220(17)]	111.87		2.07
35	N-(methylethyl)-N'-(methylethyl)-2-vinylpent-3-ene-1,5-diamide ?	113.87	238	2.30
36	4-methyl-N-(methylethyl)-N'-(methylethyl)pent-2-ene-1,5-diamide ?	118.99	226	14.61

The reaction of elimination of 2-propanamine, shown below, takes place at a lower extent compared to the elimination of ammonia from polyacrylamide, and a relatively larger amount of monomer is generated from the pyrolysis of the *N*-substituted polymer:



The level of 1-(methylethyl)piperidine-2,6-dione derivatives in the pyrolysate is lower than that of the corresponding compounds in the pyrolysate of polyacrylamide. Some of the identifications of the compounds in the pyrolysate were done only tentatively. Many of the peaks in the pyrogram shown in Figure 6.7.18 had spectra irretrievable from common mass spectral libraries. For example, the peaks eluting at 71.98 min. and 72.63 min. in the pyrogram were assigned to 1-(methylethyl)piperidine-2,6-dione and 3-methylene-1-(methylethyl)piperidine-2,6-dione, respectively. These spectra are shown in Figure 6.7.19 and Figure 6.7.20, respectively.

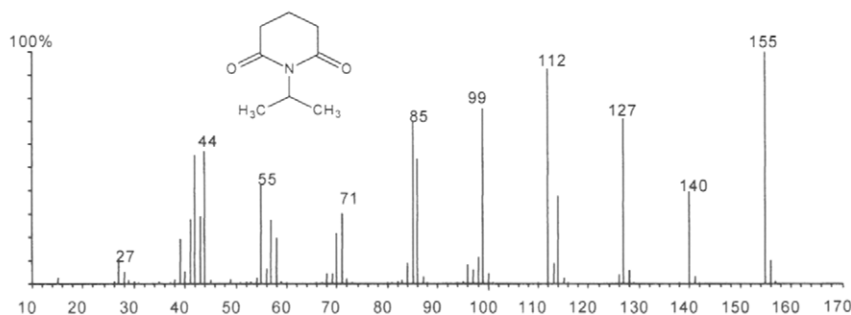


FIGURE 6.7.19. Mass spectrum assigned to 1-(methylethyl)piperidine-2,6-dione ($MW = 155$).

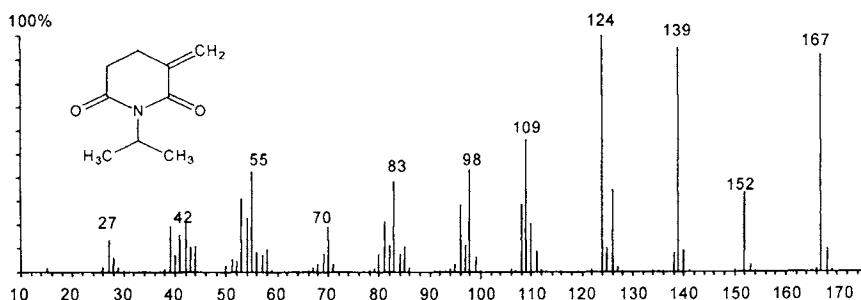


FIGURE 6.7.20. Mass spectrum assigned to 3-methylene-1-(methylethyl)piperidine-2,6-dione (MW = 167).

The similarity of compounds generated in the pyrolysis of polyacrylamide and poly(N-isopropylacrylamine) shows that the N-substituted acrylamides have basically the same pyrolysis mechanism and generate homologs of the same pyrolysis products.

- Copolymers of acrylamide

Several copolymers of acrylamide are used in practice. The addition of the acrylamide units in a copolymer can modify the polarity and bring a different hydrophilic character to the copolymer. Some pyrolysis studies on acrylamide copolymers are reported in literature [5]. Pyrolysis experiments for two copolymers of acrylamide are discussed below. The first copolymer is poly(acrylamide-co-acrylic acid) 1.5 wt % acrylic acid, CAS# 9003-06-9, with $M_w = 15,000,000$. The pyrogram of this compound is shown in Figure 6.7.21. The pyrolysis was done at 600°C in He at a heating rate of 20°C/ms. The separation was done on a Carbowax column in similar conditions as for other experiments (see also Table 4.2.2).

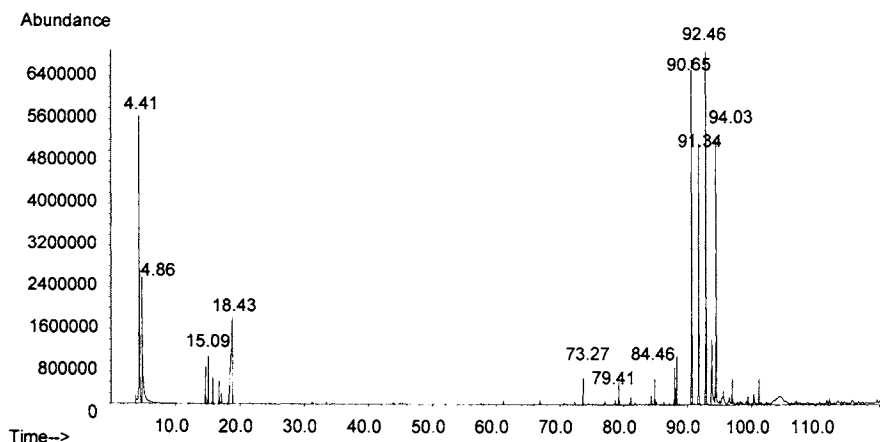


FIGURE 6.7.21. Result for a Py-GC/MS analysis of poly(acrylamide-co-acrylic acid) 1.5 wt % acrylic acid CAS# 9003-06-9, with $M_w = 15,000,000$. Pyrolysis done on 0.4 mg material at 600°C in He, with the separation on a Carbowax type column.

There are practically no differences between the pyrogram of polyacrylamide homopolymer shown in Figure 6.7.15 and that of the pyrogram shown in Figure 6.7.22. The pyrogram of poly(acrylic acid) (see Figure 6.7.2) has few truly diagnostic compounds and also contains compounds that are generated at low level in the pyrogram of polyacrylamide (see Figure 6.7.17), such as 2-propenoic acid. For these reasons, the low levels of acrylic acid do not influence enough the pyrogram of the copolymer to allow its detection.

The following Py-GC/MS results were obtained for a sample of poly(acrylamide-co-acrylic acid) potassium salt, CAS# 90363-65-8. The polymer is crosslinked and has the idealized structure $[-CH_2-CH(COOM)-]_x[-CH_2-CH(CONH_2)-]_y$ M = H, K. The pyrogram is shown in Figure 6.7.22. The pyrolysis was done similar to the sample shown above, for poly(acrylamide-co-acrylic acid) with 1.5% acrylic acid.

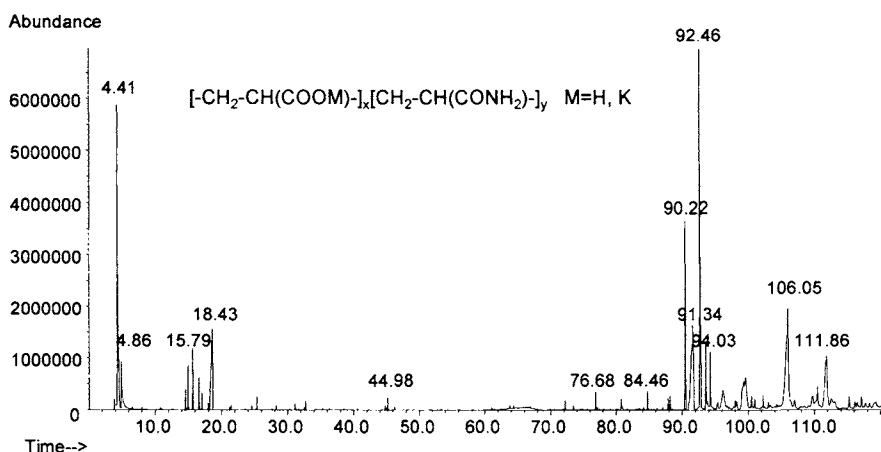


FIGURE 6.7.22. Result for a Py-GC/MS analysis of poly(acrylamide-co-acrylic acid) potassium salt (crosslinked). Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

Most of the compounds identified in the pyrogram of polyacrylamide are still present in the pyrogram of poly(acrylamide-co-acrylic acid) potassium salt. However, some compounds, such as 5-methyl-3-methylenepiperidine-2,6-dione (?), and 3-methylenepiperidine-2,6-dione (?) are at lower levels. Also, new peaks are seen at higher retention times in the pyrogram. These peaks were only tentatively identified (and typically with a relatively poor match) using their mass spectra, and they belong to 3-methyl-2(1H)-quinolinone ? MW = 159 ret. time 91.18 min., ?-dimethyl-2-(1H)-quinolinone MW = 173 ret. time 96.14 min., 1,2,3,7-tetramethylindole MW = 173 ret. time 99.57 min., 8-quinolinol MW = 145 ret. time 106.05 min., N-formyl-1,2,3,4-tetrahydroquinoline MW = 161 ret. time 110.43 min., and 2,3-dimethyl-quinolinol-4(1H)-one MW = 173 ret. time 111.86 min.. These compounds (if they were correctly identified) seem to be quinoline derivatives. Their formation may occur through eliminations and formation of aromatic cycles at high temperatures.

- Poly(acrylonitrile)

Poly(acrylonitrile) or PAN is another polymer obtained from an acrylic acid derivative. The polymer can be obtained by photopolymerization using a binary catalyst (8-acryloyloxyquinoline polymer and carbon tetrabromide), by polymerization in water at 40–50° using a peroxodisulfate-thiourea redox system [68] or using an organomagnesium catalyst. The homopolymer can be thermally converted into carbon fiber or used as is in packaging laminations, showing excellent oxygen and CO₂ barrier properties. Its copolymers are widely used in fibers, packaging laminates, or as synthetic rubber.

Thermal behavior of poly(acrylonitrile) has been studied frequently and reported in literature. Between 250° C and 280° C PAN generates 12% of products that are volatile at 25° C, consisting of HCN, acrylonitrile, and vinyl acetonitrile, and 88% of products that are nonvolatile at room temperature [69, 70]. Between 280° C and 450° C five major volatile products are detected, namely C₂N₂, HCN, acrylonitrile, acetonitrile, and vinyl acetonitrile. A nonvolatile residue also remains after the heating [71]. A different study shows that by heating between 250° C and 350° C the main products generated are NH₃ and HCN [72]. Also the formation of HCN, hydrogenated acrylonitrile, dimer and trimer, acetonitrile, and methacrylonitrile is reported during heating at 235° C [73].

Pyrolysis of polyacrylonitrile is different in some respects to that of the polyacrylamides. Initial decomposition starts at 260° with a maximum rate at 345 °C [74]. The activation energy of thermal degradation is 125.6 kJ mol⁻¹ (30 kcal mol⁻¹) as reported in one study [74] or 71.5 kJ mol⁻¹ as reported in a different study [75]. A 10% weight loss occurs at 340 °C, 30% weight loss below 400 °C, and 50% weight loss at 590 °C [76, 77]. Char residue at 600 °C is 57.7% [78]. Polyacrylonitrile is more stable than other vinyl polymers such as polystyrene, polyacrylic acid, and polyacrylamide. Pyrolysis at 600° C generates about 18.2 g of hydrogen cyanide per 100 g of polymer [79]. Heating in oxygen at approximately 150° produces an insoluble ladder polymer [80]. Activation energy of oxidative thermal degradation is 134.4 kJ mol⁻¹ (32.1 kcal mol⁻¹) [81]. A number of other studies on pyrolysis of polyacrylonitrile were reported in literature [82–84].

A pyrogram of a polyacrylonitrile sample with M_w = 86,200 is shown in Figure 6.7.23. The conditions for pyrolysis and for the analysis of pyrolysate were the same as those used for the analysis of other examples of polymers previously discussed (see Table 4.2.2). The peak identification in the pyrogram was done using MS library searches and is given in Table 6.7.13.

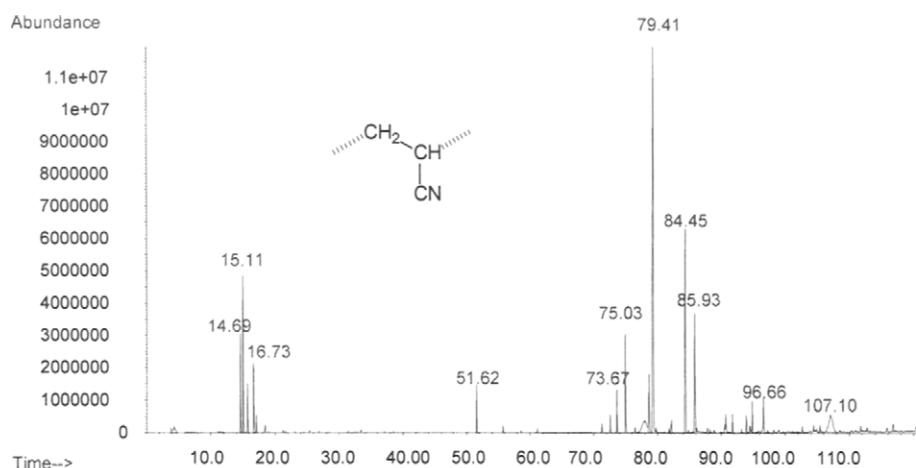


FIGURE 6.7.23. Result for a Py-GC/MS analysis of polyacrylonitrile $M_w = 86,200$. Pyrolysis done on 0.4 mg material at 600°C in He, with the separation on a Carbowax type column.

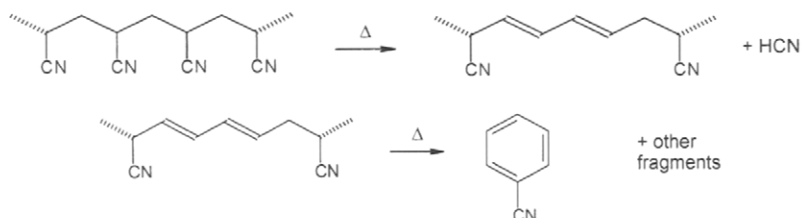
TABLE 6.7.13. Compounds identified in the pyrogram of polyacrylonitrile $M_w = 86,200$, shown in Figure 6.7.23 and obtained at 600°C .

Peak	Compound	Ret. Time	MW	Area %
1	carbon dioxide	4.36	44	1.59
2	ammonia	6.22	17	trace
3	2-methyl-2-propenenitrile	14.69	67	4.03
4	2-propenenitrile (acrylonitrile)	15.11	53	6.71
5	acetonitrile	15.79	41	2.28
6	hydrocyanic acid	16.73	27	3.42
7	propanenitrile	17.17	55	0.78
8	water	18.50	18	trace
9	1-cyano-2-butene	18.89	81	trace
10	1H-pyrrole-3-carbonitrile	51.62	92	1.98
11	benzonitrile	55.65	103	trace
12	3-methylbenzonitrile	58.55	117	trace
13	4-methylbenzonitrile	61.30	117	trace
14	3,4-dimethylbenzonitrile	66.71	131	trace
15	ethylidenepropanedinitrile	71.32	92	0.63
16	4-ethylidene-pent-2-enedinitrile	72.62	118	0.99
17	unknown [66(100), 67 (90), 120(40), 119(46), 54(33)]	73.67		2.08
18	cyclopropylmethylenepropanedinitrile	75.03	118	4.71
19	ethenylpyrazine	78.09	106	trace
20	2-methylpentanedinitrile	78.72	108	3.11
21	1-buten-2,4-dicarbonitrile	79.41	106	33.33
22	propenylpyrazine ?	82.25	120	1.25
23	pentanedinitrile	84.45	94	14.59
24	4-ethylidenepent-2-enedinitrile	85.85	118	trace
25	butanedinitrile	85.93	80	5.25
26	3-hexenedinitrile	85.98	106	2.00
27	4-heptyliminopent-2-enedinitrile	90.76	119	1.83

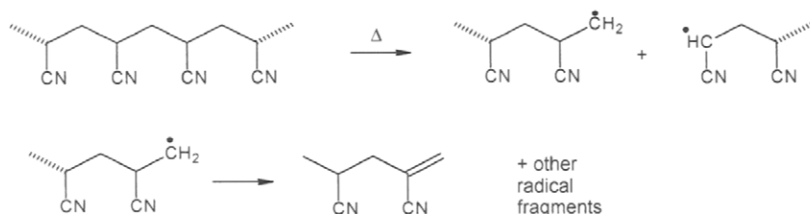
TABLE 6.7.13 (continued). Compounds identified in the pyrogram of polyacrylonitrile $M_w = 86,200$, shown in Figure 6.7.23 and obtained at 600°C .

Peak	Compound	Ret. Time	MW	Area %
28	1,4-benzendicarbonitrile	91.81	128	1.02
29	4-cyanobenzeneacetonitrile	93.20	142	0.48
30	α -dicyanotoluene	93.98	142	1.16
31	4-amino-1,2-benzenedicarbonitrile + 2,5-dicyano-3-methylpyridine ?	94.53		0.84
32	4-propylenepent-2-enedinitrile	94.92	132	1.56
33	1-hexene-2,4-dicarbonitrile	96.66	106	2.88
34	unknown [141(100), 288(71), 125(61), 94(57), 106(54), 57(50)]	107.10		1.50

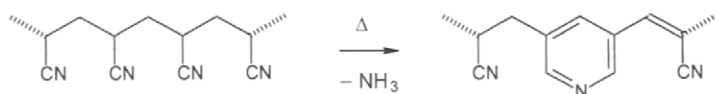
This polymer seems to decompose with some elimination of HCN from the side chain of the polymer, but the main components in the pyrolysate are various nitriles. The reactions taking place during pyrolysis are indicated schematically below (see also [23]):



The formation of 1-buten-2,4-dicarbonitrile probably occurs as follows:



The formation of pyridine cycles (see e.g. [85]) and that of traces of ammonia can be explained by reactions of the type:



The presence of pyrazine in the pyrolysate may indicate the formation of $\cdot\text{CH}_2\text{-C}\equiv\text{N}$ radicals that can form pyrazine in a termination reaction.

- Copolymers of acrylonitrile

A number of copolymers with important practical applications have acrylonitrile as comonomer. Some of these copolymers are used in acrylic fibers with the purpose of modifying specific properties such as wettability. Such copolymers are obtained, for example, with comonomers, including methyl acrylate, methyl methacrylate, vinyl acetate, or acrylamide. The copolymer of acrylonitrile with butadiene is widely used under the name of nitrile rubber in tire industry. The copolymer of acrylonitrile with styrene (SAN) is also frequently used in practice due to its good mechanical properties. A common terpolymer of acrylonitrile is ABS (acrylonitrile-butadiene-styrene copolymer). This material is easily processed and has excellent mechanical properties, reasons for which it is used to make computer and TV cabinets, domestic appliances, furniture parts, automotive parts, etc. This terpolymer is typically produced by grafting styrene and acrylonitrile directly on a polybutadiene latex in a batch or a continuous emulsion polymerization process. The degree of grafting is a function of the 1,2-vinyl content of the polybutadiene, of monomer concentrations, and of temperature. Other terpolymers include poly(acrylonitrile-co-1,3-butadiene-co-isoprene) used as a rubber substituent, poly(acrylonitrile-co-ethylene-co-styrene) or AES, poly(acrylonitrile-co-styrene-co-propylene), etc. Numerous studies regarding pyrolysis, quantitation using pyrolysis, or thermal stability of the copolymers from this group were published [86–102], etc. Some reports on thermal stability are summarized in Table 6.7.14 [6].

TABLE 6.7.14. Summary regarding literature information on thermal decomposition of several copolymers of acrylonitrile.

Polymer	Temp. °C	Results	Ref.
poly(α -chloro-acrylonitrile-co-methyl methacrylate)	>150	HCl, methyl methacrylate, α -chloroacrylonitrile	103
poly(acrylonitrile)-blend-poly(methyl methacrylate) 50/50 w/w	Up to 320	NH ₃ , HCN, methyl methacrylate	104
poly(acrylonitrile)-blend-poly(methyl methacrylate) 50/50 w/w	320–500	chain-fragment fraction and small amounts of CO, CO ₂ , methanol, CH ₄	104
poly(acrylonitrile-co-2-bromoethyl methacrylate)	below 310	ethylene, CO ₂ , vinyl bromide, acetaldehyde, 1,2-dibromoethane	105
poly(acrylonitrile-co-2-bromoethyl methacrylate) 50/50 mol/mol	310–500	propane, isobutene, CO ₂ , HCN, isocyanic acid, etc.	106
poly(acrylonitrile-co-methyl acrylate-co-vinyl bromide) 10 wt.% MA, 5 wt.% VB	180–320	CH ₃ Br, HBr, H ₂ O, CO ₂ , CH ₃ OH, NH ₃ , HCN, hydrogenated acrylonitrile, dimer, trimer, acetonitrile, methacrylonitrile, naphthyridine fragments	73
poly(acrylonitrile-co-methyl methacrylate) 1/410-1/8	220–280	only methyl methacrylate from 410/1 and 40/1 (molar ratio) copolymers; methyl methacrylate and small amounts of acrylonitrile from 16/1 and 8/1 copolymers; rapid decrease in the molecular weight of all copolymers	106
poly(acrylonitrile-co-vinyl acetate) 7.5 wt% VA	260	HCN, hydrogenated acrylonitrile, dimer, trimer, acetonitrile, methacrylonitrile, acetic acid	73

Several examples of pyrolysis results for acrylonitrile copolymers are given below. One such copolymer is poly(acrylonitrile-co-methyl acrylate), CAS# 24968-79-4. The copolymer has a relatively low level of methyl acrylate comonomer and has idealized formula $[-CH_2-CH(CN)-]_x[CH_2-CH(COOCH_3)-]_y$ ($y < x$). The pyrogram for this copolymer was obtained at 600° C in He using conditions similar to other experiments previously

presented in this book (see Table 4.2.2). The pyrogram of this copolymer is given in Figure 3.4.6. The same pyrogram is shown in Figure 6.7.24 together with that of poly(acrylonitrile), which is also given in Figure 6.7.23.

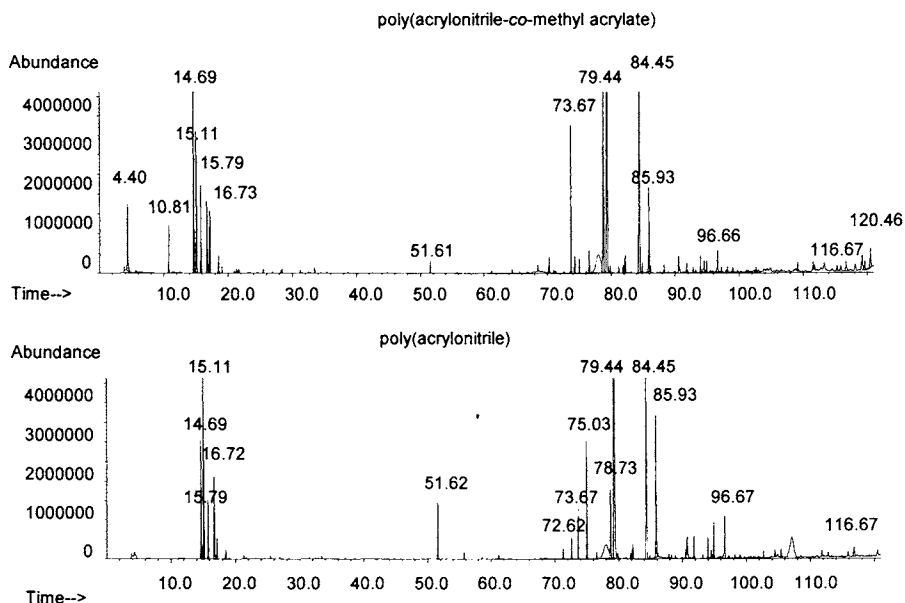


FIGURE 6.7.24. Result for a Py-GC/MS analysis of poly(acrylonitrile-co-methyl acrylate) with a relatively low level of methyl acrylate (upper trace) and of poly(acrylonitrile) (lower trace). Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

As it can be seen from Figure 6.7.24 and can be concluded after detailed comparison of the pyrograms using the data analysis capability of a mass spectrometer, the pyrogram of the copolymer is very similar to that of poly(acrylonitrile). Some variability in the peak intensities can be noticed, but the chemical nature of the pyrolysate components is basically the same. Only a few peaks are generated from the methyl acrylate moiety. In Figure 6.7.24, the peak of methanol (ret. time 10.81 min.) is noticeable and can be an indication of the nature of the copolymer. Other compounds typical for the pyrolysis of poly(methyl acrylate) also can be detected by a detailed inspection of the pyrogram. For example, the peak of 2-propenoic acid methyl ester is small but present at 12.52 min. However, the dimer and trimer of 2-propenoic acid methyl ester, which dominate the pyrolysate of poly(methyl acrylate) (see Figure 6.7.7), are not present in the pyrolysate of the copolymer. Other small differences are not diagnostic, and most of the compounds eluting at retention times higher than 100 min. were not identified.

Pyrolysis results of a common copolymer, poly(acrylonitrile-co-butadiene), with 19–22 wt % acrylonitrile, CAS# 9003-18-3, are shown in Figure 6.7.25. The idealized formula of the copolymer is $[-CH_2-CH(CN)-]_x[-CH_2CH=CHCH_2-]_y$. The pyrolysis and pyrolysate separation were done in the same conditions as those for other examples previously discussed (see Table 4.2.2). The MS was operated in EI+ mode and peak identification

was obtained using MS spectral library searches only. The results are given in Table 6.7.15.

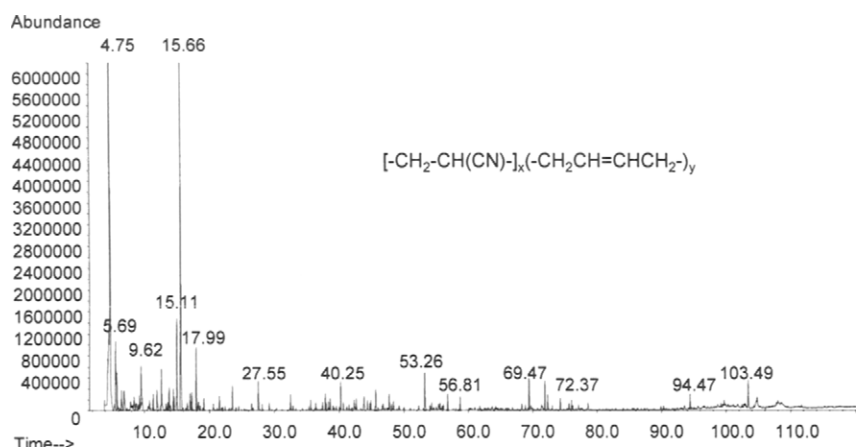


FIGURE 6.7.25. Result for a Py-GC/MS analysis of poly(acrylonitrile-co-butadiene) with 19–22 wt % acrylonitrile. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 6.7.15. Compounds identified in the pyrogram of poly(acrylonitrile-co-butadiene) with 19–22 wt % acrylonitrile shown in Figure 6.7.25.

Peak	Compound	Ret. Time	MW	Area %
1	ethane	4.37	30	trace
2	1-propene	4.43	42	2.62
3	2-methylpropene	4.55	56	trace
4	1-butene	4.59	56	trace
5	2-butene	4.62	56	7.25
6	1,3-butadiene	4.75	54	19.50
7	1,3-pentadiene	5.69	68	3.80
8	1,4-pentadiene	5.88	68	1.87
9	1,3-cyclopentadiene	6.54	66	1.15
10	1,4-hexadiene	6.89	82	1.77
11	1,3,5-hexatriene	8.46	80	0.98
12	cyclohexene	9.27	82	0.52
13	1,3-cyclohexadiene	9.62	80	2.30
14	3-methyl-1,5-heptadiene	11.41	110	0.70
15	2,6-octadiene	11.95	110	1.36
16	benzene	12.68	78	2.50
17	ethenylcyclohexane	13.85	110	1.05
18	2,2-dimethyl-4-decene	14.49	168	1.06
19	2-methyl-2-propenenitrile	14.69	67	0.72
20	2-propenenitrile (acrylonitrile)	15.11	53	4.87
21	4-ethenylcyclohex-1-ene	15.66	108	21.38
22	hydrocyanic acid	16.73	27	trace
23	propanenitrile	17.17	55	0.97
24	(Z,E)-1,3,5-octatriene	17.33	108	0.77
25	toluene	18.00	92	3.17

TABLE 6.7.15 (continued). Compounds identified in the pyrogram of poly(acrylonitrile-co-butadiene) with 19–22 wt % acrylonitrile shown in Figure 6.7.25.

Peak	Compound	Ret. Time	MW	Area %
26	2,3-dimethyl-1,3-cyclohexadiene	19.18	108	0.55
27	butanenitrile	21.57	69	0.71
28	ethylbenzene	23.57	106	1.22
29	1,4-dimethylbenzene	27.55	106	1.64
30	styrene	32.61	104	0.69
31	1,5-diethenyl-3-methyl-2-methylenecyclohexane	37.88	162	0.85
32	2-methyl-5-hexenenitrile	38.61	109	0.68
33	spiro[2.9]dodeca-4,8-diene ?	40.25	162	1.14
34	spiro[2.9]dodeca-5,9-diene ?	43.86	162	1.07
35	2,4-hexadienenitrile	44.37	93	trace
36	2,5-heptanedinitrile	45.66	122	1.12
37	2,6-diethenyl-cis-cyclooctene isomer	47.75	162	0.93
38	4-cyanocyclohexene	53.26	107	1.88
39	1H-2,3-dihydroindole	56.81	119	0.78
40	1,2,3,4-tetrahydroquinolone	58.73	133	0.64
41	naphthalene	63.87	128	trace
42	1-amino-2,4-benzene	69.28	121	trace
43	?-methylcycloheptyl-?,?-dicarbonitrile ?	69.47	160	1.37
44	?-methylcycloheptyl-?,?-dicarbonitrile ?	71.93	160	1.43
45	?-methylcycloheptyl-?,?-dicarbonitrile ?	72.37	160	0.77
46	2-methylpentanedinitrile	78.72	108	trace
47	tetradecanenitrile	94.47	209	0.71
48	heptadecanenitrile	103.49	251	1.51

The analysis of pyrolysate of poly(acrylonitrile-co-butadiene) indicated in Table 6.7.15 shows the presence of compounds generated from the acrylonitrile sequences, from butadiene sequences, as well as compounds generated from the joining groups of the polymer. Comparing the pyrolysis composition of the copolymer with that of poly(acrylonitrile) shown in Figure 6.7.23, it can be seen that several major small molecules from poly(acrylonitrile) pyrolysate such as 2-methyl-2-propenenitrile, 2-propenenitrile (acrylonitrile), propanenitrile, etc. are present in the copolymer pyrolysate. Also, comparing the pyrolysis composition of the copolymer with that of poly(1,3-butadiene) shown in Figure 7.1.1, it can be seen that many compounds are identical in the two pyrolysates. In addition to that, compounds such as 2-methyl-5-hexenenitrile, tetradecanenitrile, or heptadecanenitrile are very likely formed, including fragments from both comonomers. This shows that the copolymer has a random structure. A more detailed analysis of sequence distribution (determination of the run number) would be possible if a quantitative study of the relative yield of monomers were done on the pyrolysate (see Section 4.3). However, the yield of different compounds in the pyrolysate, although in principle proportional to the amount of the corresponding comonomer in the copolymer, is affected by different proportionality factors. In addition to that, the sensitivity of the MS detector is not the same for different compounds. For these reasons, only a rough estimate of the polymer composition can be obtained from pyrolysis data. For the volatile compounds seen in poly(acrylonitrile-co-butadiene) pyrolysate in the experimental conditions previously described, the proportion of compounds not containing nitrogen can be estimated as representing about 85% (mol) from the total area in the chromatogram, and the proportion of compounds containing nitrogen at about 15% (mol). These proportions are not too far from the value of 19–23 wt% acrylonitrile in the copolymer (since butadiene has MW = 54 and acrylonitrile has MW = 53, the same proportion is practically kept for their molecular ratio), which

indicates that the ratio of non-nitrogenous vs. nitrogenous molecules in the pyrolysate is roughly kept close to that of the two comonomers.

In the case of a low content of a comonomer in a copolymer, the peak characteristics for fragment molecules generated from the comonomer or comonomer sequences can be very small. Since most pyrograms are very complex, with hundreds of small components, it is in many instances difficult to assign a particular compound to a low level comonomer. This is, for example, the case of the pyrolysis of the terpolymer poly(acrylonitrile-co-butadiene-co-acrylic acid) dicarboxy terminated 18 wt % acrylonitrile, 2.4 carboxyl/molecule, CAS# 68891-50-9. No peaks characteristic for the acrylic acid are seen in the pyrogram.

Pyrolysis results for a terpolymer, poly(acrylonitrile-co-butadiene-co-styrene) high butadiene content CAS# 9003-56-9, are shown in Figure 6.7.26. The idealized formula of the copolymer is $[-CH_2-CH(C_6H_5)-]_x[-CH_2-CH(CN)-]_y(-CH_2CH=CHCH_2)_z$. The pyrolysis and pyrolysate separation were done in the same conditions as those for other examples previously discussed (see Table 4.2.2). The MS was operated in EI+ mode and peak identification was obtained using MS spectral library searches only. The results are given in Table 6.7.16.

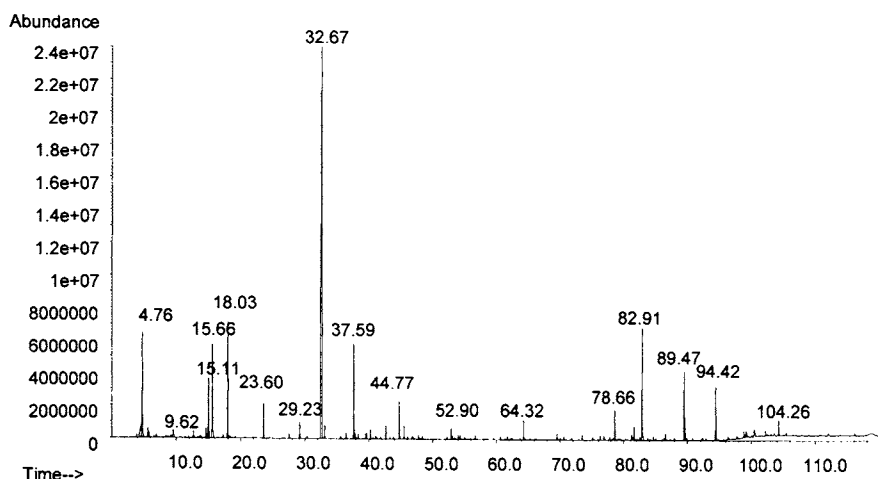


FIGURE 6.7.26. Result for a Py-GC/MS analysis of poly(acrylonitrile-co-butadiene-co-styrene) high butadiene content. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 6.7.16. Compounds identified in the pyrogram of poly(acrylonitrile-co-butadiene-co-styrene) high butadiene content shown in Figure 6.7.26.

Peak	Compound	Ret. Time	MW	Area %
1	ethane	4.37	30	trace
2	1-propene	4.43	42	trace
3	2-methylpropene	4.55	56	trace
4	1-butene	4.59	56	trace
5	2-butene	4.62	56	1.49
6	1,3-butadiene	4.76	54	5.84
7	1,3-pentadiene	5.66	68	0.35
8	1,3-cyclohexadiene	9.62	80	0.77
9	benzene	12.68	78	0.49
10	2-methyl-2-propenenitrile	14.69	67	0.63
11	2-propenenitrile (acrylonitrile)	15.11	53	3.82
12	4-ethenylcyclohex-1-ene	15.66	108	5.31
13	hydrocyanic acid	16.73	27	trace
14	toluene	18.03	92	7.43
15	ethylbenzene	23.60	106	1.83
16	1,2-dimethylbenzene	27.58	106	trace
17	propylbenzene	29.23	120	0.83
18	ethenyl benzene (styrene)	32.67	104	42.05
19	1-propenylbenzene	33.15	118	0.57
20	α -methylstyrene (1-methylethenyl)benzene	37.59	118	5.08
21	spiro[2.9]dodeca-4,8-diene ?	40.25	162	0.41
22	2-methyl-5-hexenenitrile	41.97	109	trace
23	2-propenylbenzene	42.59	118	0.65
24	1-phenyl-1-butene	44.77	132	1.74
25	1-ethenyl-4-ethylbenzene	45.50	132	0.66
26	1,4-divinylbenzene	52.90	130	0.52
27	1,3-divinylbenzene	54.03	130	trace
28	1-ethenyl-2,3-dihydro-1H-indene	54.33	144	trace
29	(1-methylpent-3-enyl)benzene	54.50	160	trace
30	(4-methyl-1-methylenepent-4-enyl)benzene	61.73	172	trace
31	3-cyclohexen-1-yl-benzene	64.32	158	0.97
32	2-methylnaphthalene	69.55	142	trace
33	α -methylenebenzeneacetonitrile	70.58	129	trace
34	1-methylnaphthalene	71.86	142	trace
35	benzeneacetonitrile	73.49	117	trace
36	1,1'-biphenyl	76.91	154	trace
37	4-phenylpent-2-enenitrile	78.66	157	1.68
38	1-phenyl-3,4-divinyl-cyclohexane	81.64	212	0.63
39	benzenebutanenitrile	82.91	145	6.89
40	pentanedinitrile	84.45	94	trace
41	3-phenyl-2-propenenitrile	84.66	129	trace
42	unknown or mixture	86.55		0.33
43	1,1'-(1,3-propanediyl)bis-benzene	89.47	196	3.75
44	2,4-dimethylquinoline	89.62	157	1.21
45	2,4-diphenylpentene	92.32	222	trace
46	3-phenylbut-3-enyl)benzene or styrene dimer	94.42	208	2.88
47	1,2-diphenylcyclopropane	100.46	194	0.13
48	1,1'-(1-butene-1,4-diyl)bisbenzene	102.26	208	trace
49	2,5-diphenylhex-1-ene	104.26	236	1.05

The polymer pyrolysate contains all three monomers, 1,3-butadiene (A), ethenyl benzene (B), and 2-propenenitrile (C), which indicates the material is a terpolymer. Also, traces of BB dimer and traces of CC type are present (the dimer of 1,3-butadiene

was not detected in the pyrolysate of the corresponding homopolymer). Also mixed dimers such as (1-methylpent-3-enyl)benzene (AB) (MW = 160), 2-methyl-5-hexenenitrile (AC) (MW = 109), and 4-phenylpent-2-enenitrile (BC) (MW = 157) are present in the pyrolysate. This shows the random nature of the polymer, and the quantitation of the levels of monomers and dimers could be used for the understanding of the polymer structure.

Other copolymers of acrylonitrile were previously discussed, such as poly(vinyl chloride-co-acrylonitrile) (see e.g. Figure 6.3.4). Also, various other studies on acrylonitrile copolymers are reported in literature [107, 108].

- Other polymers of acrylic acid derivatives

Some results on thermal stability and thermal decomposition products of other acrylic acid derivatives including poly(α -chloro-acrylonitrile), poly(α -phenyl acrylonitrile), and poly(acryloyl chloride) as reported in literature are given in Table 6.7.17 [6].

TABLE 6.7.17. Summary regarding literature information on thermal decomposition of poly(α -chloro-acrylonitrile), poly(α -phenyl acrylonitrile) and poly(acryloyl chloride).

Polymer	Temp. °C	Results	Ref.
poly(α -chloroacrylonitrile)	150-200	HCl	109
poly(α -chloroacrylonitrile)	ambient to 500	HCl and small amount of HCN at higher temperatures	110
poly(α -phenylacrylonitrile)	ambient to 500	high yields of monomer	110
poly(acryloyl chloride)	ambient to 500	acrylic acid, HCl, H ₂ O, CO, acryloyl chloride, 3,5-(6-chloro-2-pyrone) and fragments thereof, C ₆ , C ₉ , C ₁₂ , C ₁₅ fragments	55

- Poly(methacrylic acid)

Poly(methacrylic acid) or poly(2-methyl-2-propenoic acid), $[-CH_2C(CH_3)(COOH)]_n$, has properties and utilizations rather similar to those of poly(acrylic acid). The material is obtained by radical polymerization and is typically found in atactic form (CAS# 25087-26-7). The stereospecific forms also are known (syndiotactic CAS# 25750-36-1, or isotactic CAS# 25068-55-7). Poly(methacrylic acid) is a weak acid polyelectrolyte. It is used as an adhesive, a binder for ceramic materials, for various coatings [1, 19, 111–115] in corrosion inhibitor formulations, for delayed-release medication; as a dispersant; as an additive to soap and detergents; and as a thickener. It is used in cosmetics, textile industry, medical technology, etc. Similar to poly(acrylic acid), the salts of poly(methacrylic acid) are used in textile finishing, leather treatment, water purification, pigment dispersants, paper sizing, coatings of drugs and seeds, industrial cleaners, etc.

The thermal decomposition of poly(methacrylic acid) starts at about 200° when it eliminates water and some monomer, leaving a residue of poly(methacrylic anhydride) [116]. Some decarboxylation also is noticed at lower temperatures. At higher temperatures the decomposition is more complex [117]. The water elimination process has an activation energy of 40.5 kcal mol⁻¹, and the fragmentation of the anhydride an activation energy of 37.4 kcal mol⁻¹ [118].

The salts of poly(methacrylic acid) with Na, Li, K and Cs (CAS# for Na salt 25086-62-8) decompose at approximately 350°, whereas the Mg and other alkaline earth metal salts decompose at 500°. The NH₄ salt decomposes somewhat differently with elimination of NH₃, H₂O, and other fragments, at higher temperatures (500° C) forming some isocyanic acid and HCN [119]. Some results on poly(methacrylic acid) thermal decomposition as reported in literature are given in Table 6.7.18 [6].

TABLE 6.7.18. Summary regarding literature information on thermal decomposition of poly(methacrylic acid).

Polymer	Temp. °C	Results	Ref.
poly(methacrylic acid ammonium salt)	ambient to 500	isocyanic acid, NH ₃ , HCN, isobutene, CO ₂ , (trace), methacrylonitrile (trace)	120
poly(methacrylic acid Li, Na, K and Co salts)	ambient to 500	ethylene, 1-butene, isobutene, acetylene, CO ₂ , CH ₄ , CO, acetone, isopropylaldehyde, methacrolein, butyraldehyde, methyl ethyl ketone, benzene (trace), methyl isopropyl ketones, methyl isopropenyl ketone, diethyl ketone, methyl n-propenyl ketone, cyclopentanone, methyl cyclopentanone, dimethyl cyclopentanone, dimethyl cyclopentenone and traces of toluene, di-isopropyl ketone, mesitylene, mesityl oxide CO ₂ , dimethyl ketene, trace amounts of CO, CH ₄ , isobutene, 1-butene, ethylene, acetylene, benzene, toluene, isobutyraldehyde, methyl ethyl ketone, methyl isopropenyl ketone, diethyl ketone, methyl isopropenyl ketone, di-isopropyl ketone, cyclopentanone, 2-methyl cyclopentanone, 2,5-dimethylcyclopentanone, 2,5-dimethylcyclopent-3-ene-1-one, methacrolein, butyraldehyde	121, 122
poly(methacrylic acid Mg, Ca, Sr, Ba salts)	ambient to 500	almost quantitative yields of H ₂ O, traces of monomer, residue of poly(methacrylic anhydride)	123
poly(methacrylic acid)	200	CO ₂ , propene, butenes, pentenes, pentadienes, hexene, hexadienes, hexatrienes, benzene, toluene, heptene, heptatriene, methacrylic acid, xylene, octatriene, octadiene, nonatriene, hexenedienoic acid, decatene, decatetraene, decapentaene, undecatriene, methylbenzoic acids, trimethylbenzoic acid	124
poly(methacrylic acid)	900		125

As seen from Table 6.7.18, the thermal decomposition of poly(methacrylic acid) generates at lower temperature the anhydride, and at higher temperatures undergoes decarboxylation. It can be assumed that the process leads to the formation of unsaturated chains that further decompose to form small hydrocarbon molecules and some aromatic compounds. Residual carboxyl groups may be retained on some of these molecules.

- Poly(methacrylic acid esters)

The polymers of methacrylic acid esters $[-CH_2C(CH_3)(COOR)-]_n$ are very common. Their frequent use in practice led to numerous studies of their thermal stability and of the decomposition products upon thermal decomposition. A number of analytical pyrolysis studies are reported in literature [25, 126–143].

The thermal behavior of several poly(methacrylic acid esters) evaluated for practical purposes, including heating conditions at low temperature and prolonged time, are listed in Table 6.7.19 [6].

TABLE 6.7.19. Summary regarding the literature reports on thermal decomposition of poly(methacrylic acid esters).

Polymer	Temp. °C	Results	Ref.
poly(methacrylic acid 1,2-dimethylpropyl ester)	250	monomer and small amount of olefin by side chain cracking	144
poly(methacrylic acid 1,3-dimethyl-butyl ester)	250	monomer and small amount of olefin by side chain cracking	144
poly(methacrylic acid 2,2,2-trichloroethyl ester)	600	CO ₂ , propene, vinyl chloride, vinylidene chloride	36
poly(methacrylic acid 2,2,2-trichloroethyl ester)	240	1,2-dichloroethene, chloroform, methyl methacrylate, methacrylic acid, 2,2,2-trichloroethanol, 2,2,2-trichloroethyl acrylate, 2,2,2-trichloroethyl methacrylate, 2,2-dichloroethyl methacrylate, CH ₂ =C(CH ₃)-COOCH=CCl ₂ or CH ₂ =C(CH ₃)-COOCCl=CHCl	145
poly(methacrylic acid 2,2,2-trifluoro-ethyl ester)	ambient to 500	monomer, CO ₂ , CO, CH ₄ , ethene, formaldehyde, isobutene, methyl vinyl ether, methanol	146
poly(methacrylic acid 2,2,2-trifluoro-ethyl ester)	600	CO ₂ , vinylidene fluoride, trifluoroacetaldehyde, trifluoroethanol, monomer	147
poly(methacrylic acid 2,2-dichloroethyl ester)	242	monomer (90.7%), chloroacetaldehyde (8%), 1,1,2-trichloroethane (0.5%), 2,2-dichloroethanol, methacrylic acid (0.1%), 2-chloroethylene methacrylate (0.1%)	148
poly(methacrylic acid 2,3-dibromo-propyl ester)	600	CO ₂ , propene, acetaldehyde, methyl bromide, butene, ethyl bromide, bromocyclopropane or 2-bromopropane	34
poly(methacrylic acid 2-bromoethyl ester)	ambient to 500	2-bromoethyl methacrylate (> 95%), CO ₂ (< 1%), vinyl bromide (< 1%)	149
poly(methacrylic acid 2-bromoethyl ester)	600	CO, CO ₂ , propene, acetaldehyde, methyl bromide, butene, vinyl bromide, ethyl bromide, methyl methacrylate	150
poly(methacrylic acid 2-chloroethyl ester)	600	CO ₂ , propene, acetaldehyde, vinyl chloride, ethyl chloride, monomer	36.
poly(methacrylic acid 2-chloroethyl ester)	268	monomer (99%), traces of acetaldehyde, methyl methacrylate, 1,2-dichloroethane, ethylene methacrylate	148
poly(methacrylic acid 2-fluoroethyl ester)	600	CO ₂ , vinyl fluoride, acetaldehyde, fluoroacetaldehyde	147
poly(methacrylic acid 2-hydroxy-ethyl ester)	375–500	2-hydroxyethyl methacrylate (20% at 500° C), ethylene dimethacrylate (6% at 500° C)(main products), ethylene glycol, 3-methyl-5-hydroxy-δ-valerolactone (probably), 1,2-di-isopropenyl-oxyethane (probably), CO, CO ₂ , methane, ethylene, ethane, propane, H ₂ O	151
poly(methacrylic acid 2-methoxy-ethyl ester)	ambient to 300	monomer, CO ₂	146
poly(methacrylic acid 2-sulfoethylester)	50–600	CO, CO ₂ , H ₂ O, SO ₂ , ethene	34
poly(methacrylic acid 3,3-dimethyl-butyl ester)	250	monomer	144
poly(methacrylic acid allyl ester)	ambient to 500	CO ₂ , CH ₄ , CO, H ₂ , propene, isobutene, dimethyl ketene, acrolein, diallyl ether, allyl methacrylate monomer and dimer, chain fragments including anhydride structures from side-group cyclization, and an aliphatic ketone in the vicinity of unsaturation	152
poly(methacrylic acid bisphenol S ester)	464	CO ₂ , SO ₂ , phenol, bisphenol S, hydroquinone, fragments of backbone, benzene sulfonic acid	153
poly(methacrylic acid ethyl ester)	250	monomer	144

TABLE 6.7.19 (continued). Summary regarding the literature reports on thermal decomposition of poly(methacrylic acid esters).

Polymer	Temp. °C	Results	Ref.
poly(methacrylic acid ethyl ester)	245	monomer, ethanol, ethanoic acid	145
poly(methacrylic acid glycidyl ester)	ambient to 500	CO, CO ₂ , dimethyl ketene, isobutene, propene, acrolein, allyl alcohol, glycidyl methacrylate, glycidol, short chain fragments with some unsaturation	154
poly(methacrylic acid hexafluoro-isopropyl ester)	600	CO ₂ , trifluoroacetaldehyde, acetaldehyde, 1,1,1,3,3,3-hexafluoropropane, hexafluoroisopropyl formate	147
poly(methacrylic acid isoamyl ester)	250	monomer	144
poly(methacrylic acid isobutyl ester)	250	monomer	155
poly(methacrylic acid isopropyl ester)	250	monomer	144
poly(methacrylic acid methyl ester)	170–300	100% monomer	156, 157
poly(methacrylic acid methyl ester)	246–400	as temperature is raised, fragmentation increases to give complex series of products and the monomer yield decreases	42
poly(methacrylic acid methyl ester)	160	100% monomer under 253.7 nm radiation	158
poly(methacrylic acid methyl ester)	100–400	under 254 nm radiation; 100% monomer	159
poly(methacrylic acid n-amyl ester)	250	monomer	144
poly(methacrylic acid n-butyl ester)	250	40% monomer and traces of 1-butene	155
poly(methacrylic acid n-butyl ester)	170	100% monomer under 253.7 nm radiation	155
poly(methacrylic acid n-butyl ester)	250	40% monomer and traces of 1-butene	160
poly(methacrylic acid n-propyl ester)	250	monomer	144
poly(methacrylic acid neopentyl ester)	250	monomer	144
poly(methacrylic acid phenyl ester)	ambient to 500	monomer, some CO ₂	161
poly(methacrylic acid sec-butyl ester)	250	monomer and small amounts of olefin by side-chain cracking	144
poly(methacrylic acid sec-butyl ester)	250	monomer and small amount of olefin by cracking of side chain	155
poly(methacrylic acid tert-butyl ester)	180–200	high yields of isobutylene and water, 1% monomer, trace of methacrylic acid, residue of poly(methacrylic anhydride)	162
poly(methacrylic acid tert-butyl ester)	<180	100% monomer under 253.7 nm radiation	144, 162
poly(methacrylic acid tert-butyl ester)	slow heating	changes to the anhydride via the acid on heating, decomposition yields 100% monomer	144, 163
poly(methacrylic acid tert-butyl ester)	180–200	high levels of isobutylene and water, low levels of monomer, traces of methacrylic acid, a residue of polymethacrylic anhydride	155, 162
poly[α,ω -(diethylene-glycol phthalate)dimethacrylate]	300	monomer	164
poly[α,ω -(diethylene-glycol phthalate)dimethacrylate]	400	monomer, phthalic anhydride, diethylene glycol, C ₂ H ₄ , propylene, CO ₂	164

Poly(methyl methacrylate) is probably the most utilized polymeric methacrylate. The result for flash pyrolysis using Py-GC/MS analysis of a sample of poly(methyl methacrylate), CAS# 9011-14-7, with $M_w = 15,000$ is shown in Figure 6.7.27. The pyrolysis was done in similar conditions to other examples, namely at 600°C in He at a heating rate of 20°C/ms with the separation on a Carbowax column (see Table 4.2.2) and MS detection. The peak identification for the chromatogram shown in Figure 6.7.27 was done using MS spectral library searches and is given in Table 6.7.20.

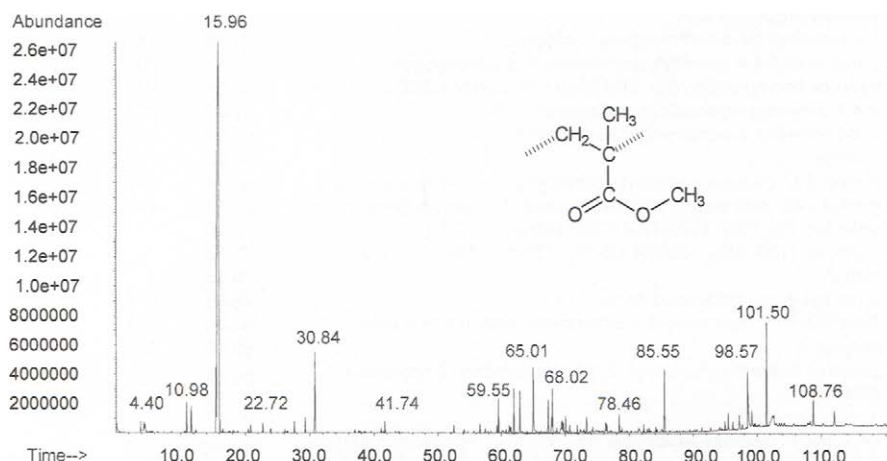


FIGURE 6.7.27. Result for a Py-GC/MS analysis of poly(methyl methacrylate) $M_w = 15,000$. Pyrolysis done on 0.4 mg material at 600°C in He, with the separation on a Carbowax type column.

TABLE 6.7.20. Compounds identified in the pyrogram of poly(methyl methacrylate) $M_w = 15,000$ shown in Figure 6.7.27. (Some compounds from the pyrogram are the result of a hydrocarbon contamination and are indicated by *).

Peak	Compound	Ret Time	MW	Area %
1	carbon dioxide	4.40	44	1.29
2	2-methylpropene	4.55	56	trace
3	2-methylbutadiene	5.30	68	trace
4	methyl formate	10.60	60	trace
5	methanol	10.68	32	trace
6	propanoic acid methyl ester	10.98	88	1.18
7	2-methylpropanoic acid methyl ester	11.69	102	1.31
8	2-propenoic acid methyl ester	12.35	86	trace
9	2-methyl-2-propenoic acid methyl ester (monomer)	15.96	100	58.58
10	2-methylenebutanoic acid methyl ester	20.45	114	trace
11*	undecane	20.86	156	0.40
12	2-methyl-3-butenic acid methyl ester	22.72	114	0.39
13	2,4-dimethyl-4-pentenoic acid methyl ester	29.32	142	0.59
14*	dodecane	27.60	170	0.49
15*	1-dodecene	30.84	168	3.95
16	methyl 1-cyclohexene-1-carboxylate	41.74	140	0.43

TABLE 6.7.20 (continued). Compounds identified in the pyrogram of poly(methyl methacrylate) $M_w = 15,000$ shown in Figure 6.7.27. (Some compounds from the pyrogram are the result of a hydrocarbon contamination and are indicated by *).

Peak	Compound	Ret Time	MW	Area %
17	pentanedioic acid dimethyl ester	52.56	160	0.29
18	2,4-dimethylpentanedioic acid dimethyl ester	56.64	188	0.41
19	2-pentenedioic acid dimethyl ester	59.55	158	1.35
20	2-methylpropenoic acid	60.09	86	trace
21	1,2-dimethyl-1,2-dicarboxymethylcyclopropane	61.98	186	1.86
22	2-methylene-4,4-dimethylpentanedioic acid dimethyl ester	62.91	200	1.80
23	hydrocarbon type [55(100), 69(100), 83(98), 97(85), 202(55), 111(47)]	65.01	202	3.53
24	2,4,4-trimethylpentanedioic acid dimethylester	67.33	202	1.50
25	2,4,4-trimethyl-2-pentenedioic acid dimethyl ester	67.86	200	trace
26	mixture	68.02		2.49
27	methyl 2-[2-(methoxycarbonyl)-2-methylcyclopropyl]propanoate	69.54	200	0.53
28	methyl 2-[2-(methoxycarbonyl)-2,2-dimethylcyclopropyl]propanoate	69.71	214	trace
29	unknown [69(100), 112(41), 41(35), 140(20), 97(11)]	70.70		0.41
30	unknown [139(100), 182(58), 95(58), 123(55), 154(32), 73(23)]	73.35		0.65
31	mixture	76.35		0.89
32*	2-methyl-2-propenoic acid dodecyl ester	78.46	254	0.71
33	1-methyl-3-cyclopentene-1,3-dicarboxylic acid dimethyl ester	82.30	198	0.39
34*	docosane	85.55	310	2.84
35	dimethyl 4-(methoxycarbonyl)-2,4,6,6-tetramethyl-2-heptene-1,7-dioate	95.52	300	0.85
36*	dodecanoic acid	98.57	200	3.82
37	dimethyl 4-(methoxycarbonyl)-4,6,6-trimethyl-2-methyleneheptane-1,7-dioate	101.50	300	4.49
38*	dodecanoic acid undecyl ester	108.76	354	1.60
39	unknown [100(100), 300(59), 213(59), 131(59), 113(55), 55(52)]	112.02		0.99

Some of the peak assignments in Table 6.7.20 are tentative because the mass spectra of many compounds in poly(methyl methacrylate) pyrolysate are not available in the commercial mass spectral libraries. For example, 2-methylene-4,4-dimethylpentanedioic acid dimethyl ester (MW = 200) and 2,4,4-trimethyl-2-pentenedioic acid dimethyl ester (MW = 200) were assigned based on the mass spectra shown in Figures 6.7.28 a and 6.7.28 b.

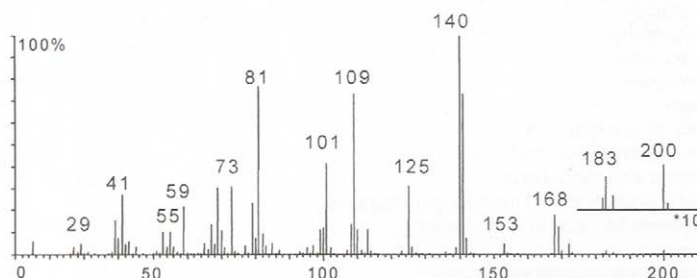


FIGURE 6.7.28 a. Tentatively assigned spectrum for 2-methylene-4,4-dimethylpentanedioic acid dimethyl ester (ret. time 62.91 min.)

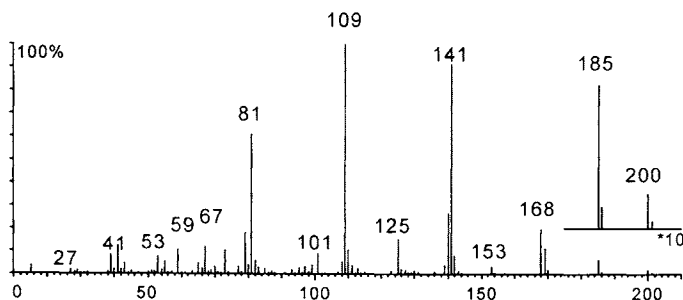


FIGURE 6.7.28 b. Tentatively assigned spectrum for 2,4,4-trimethyl-2-pentendioic acid dimethyl ester (ret. time 67.86 min.).

The only similar compound with the available spectrum in the library (NIST'98) was that of 2-methyl-3-methylenehexanedioic acid dimethyl ester (MW = 200), with the spectrum shown for comparison in Figure 6.7.29.

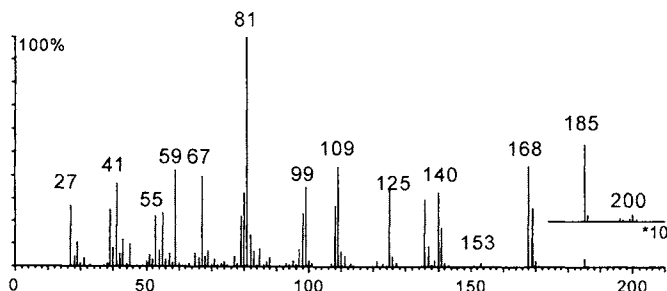


FIGURE 6.7.29. Spectrum of 2-methyl-3-methylenehexanedioic acid dimethyl ester (from NIST'98 mass spectral library).

The assignment is even more difficult as the MW of the compounds increases. The mass spectrum tentatively assigned for dimethyl 4-(methoxycarbonyl)-4,6,6-trimethyl-2-methyleneheptane-1,7-dioate (MW = 300) is shown in Figure 6.7.30. This spectrum is closely related to the mass spectrum of dimethyl 4-(methoxycarbonyl)-2-methyleneheptane-1,7-dioate previously shown in Figure 6.7.5. Differences in the mass of different fragment ions corresponding to three, two, or one CH_2 groups or to a CH_3 group can be noticed by comparing the two spectra.

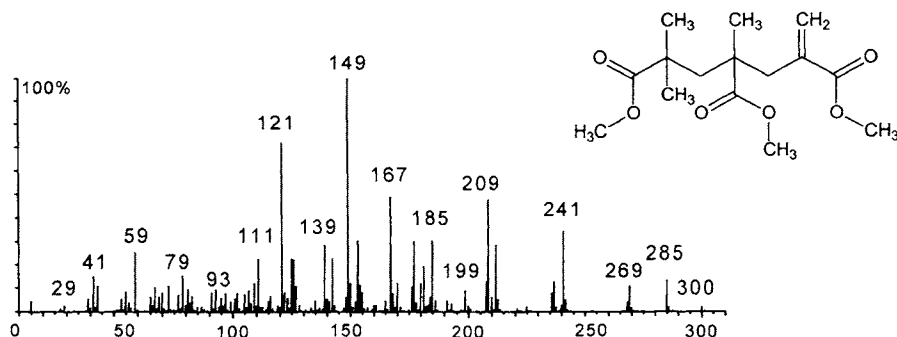
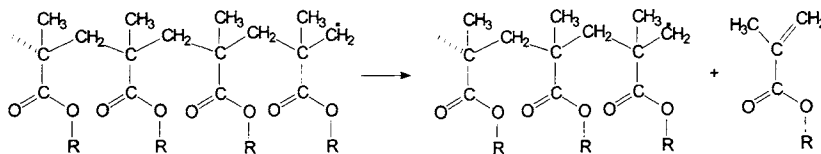


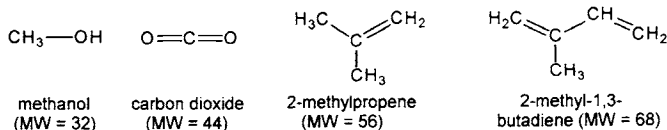
FIGURE 6.7.30. Spectrum tentatively assigned to dimethyl 4-(methoxycarbonyl)-4,6,6-trimethyl-2-methyleneheptane-1,7-dioate MW = 300 (ret. time 101.50 min.).

A number of peaks present in the pyrogram shown in Figure 6.7.27 were identified as long chain hydrocarbons, long chain acid such as dodecanoic acid or esters such as 2-methyl-2-propenoic acid dodecyl ester and dodecanoic acid undecyl ester. It is possible that these compounds are generated from the additives (or contaminants) of the polymer. Similar hydrocarbons were detected during the pyrolysis of poly(2-hydroxyethyl methacrylate) (see Figure 6.7.41).

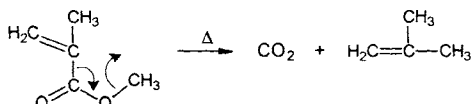
Pyrolysis of poly(methyl methacrylate) occurs with a significant proportion of monomer formation. Table 2.1.1. indicates 95% monomer yield, while the results from Table 6.7.20 show only about 59%. The disparity is caused by the differences in the pyrolysis conditions. As shown in Section 2.1, the thermal decomposition of poly(methacrylate esters) is dominated by unzipping, which is a radical propagation reaction with the cleavage of the bond in β -position to the atom bearing the unpaired electron and also β to the double carbonyl bond. This reaction leads to the formation of monomer as shown below ($R = CH_3$ for the methyl ester):



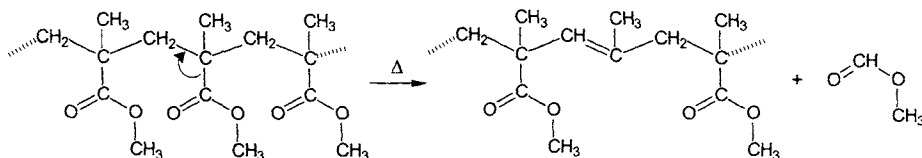
Other fragments seen in the pyrogram of poly(methyl methacrylate) and given in Table 6.7.20 include smaller fragments than the monomer. They are the result of backbone fragmentation followed by other reactions such as methanol elimination and decarboxylation of the resulting acid. Some examples of small molecules are shown below:



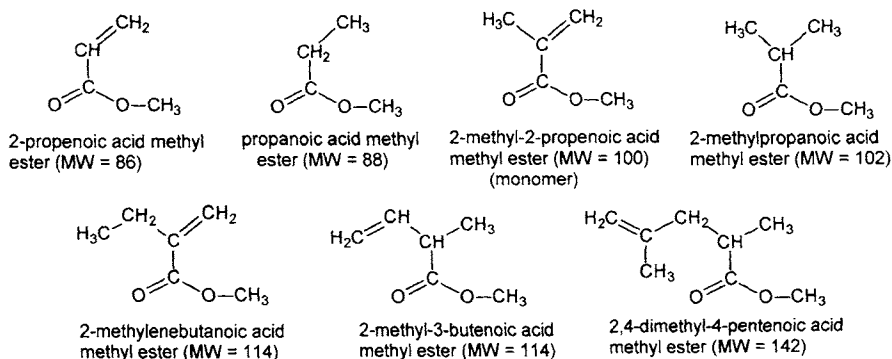
The reaction of formation of 2-methylpropene is probably a result of an elimination from methyl methacrylate, although free acids are much easier decarboxylated compared to the esters. The reaction is shown below:



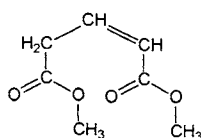
This reaction of decarboxylation is favored thermodynamically, being characterized by the following equilibrium values: ΔH_f^0 (methyl methacrylate) = -76.9 kcal mol⁻¹, ΔS_f^0 (methyl methacrylate) = 89.1 cal T⁻¹ mol⁻¹, ΔH_f^0 (CO₂) = -94.05 kcal mol⁻¹, ΔS_f^0 (CO₂) = 51.1 cal T⁻¹ mol⁻¹, ΔH_f^0 (2-methylpropene) = -4.2 kcal mol⁻¹, ΔS_f^0 (2-methylpropene) = 74.5 cal T⁻¹ mol⁻¹. This leads for the reaction to $\Delta H^0 = -21.35$ kcal mol⁻¹ and $\Delta S^0 = 36.5$ cal T⁻¹ mol⁻¹. The reaction of elimination of methyl formate followed by further cleavage of the backbone with formation of 2-methylpropene and 2-methyl-1,3-butadiene is not excluded since methyl formate is generated in the pyrolysate. However, methyl formate is present in very low level, even lower than that of 2-methylpropene or 2-methyl-1,3-butadiene. The reaction of methyl formate elimination is shown schematically below:



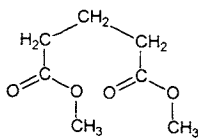
Besides the monomer, a number of other fragments with one ester group are seen in the pyrolysate. They may be the result of the cleavage of a different bond from that forming the monomer or may be due to hydrogen migrations or the rearrangement of the resulting fragment. Some examples of this type of molecule (including for comparison the monomer) are shown below in the increasing order of their MW:



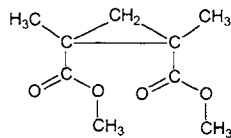
Fragments containing two ester groups are also present in the pyrogram. Some of these fragment molecules are shown below in the increasing order of their MW:



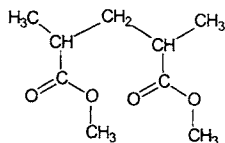
2-pentenedioic acid dimethyl ester (MW = 158)



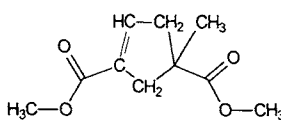
pentandioic acid dimethyl ester (MW = 160)



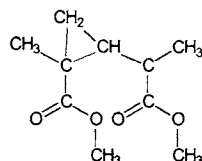
1,2-dimethyl-1,2-dicarboxymethyl cyclopropane (MW = 186)



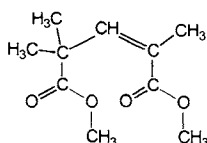
2,4-dimethylpentandioic acid dimethyl ester (MW = 188)



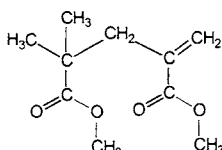
1-methyl-3-cyclopentene-1,3-dicarboxylic acid dimethyl ester (MW = 198)



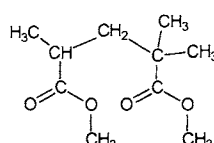
methyl 2-[2-(methoxycarbonyl)-2-methylcyclopropyl]propanoate (MW = 200)



2,4,4-trimethyl-2-pentandioic acid dimethyl ester (MW = 200)

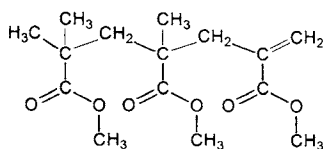


2-methylene-4,4-dimethyl pentandioic acid methyl ester (MW = 200)

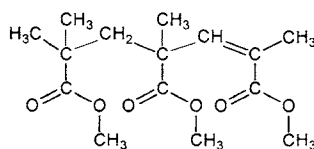


2,4,4-trimethylpentandioic acid dimethyl ester (MW = 202)

In the particular conditions used for the analysis of pyrolysate shown in Figure 6.7.27, only compounds having up to three ester groups are identifiable. Two of these compounds are shown below:



dimethyl 4-(methoxycarbonyl)-4,6,6-trimethyl-2-methyleneheptane-1,7-dioate (MW = 300)



dimethyl 4-(methoxycarbonyl)-2,4,6,6-tetramethylhept-2-ene-1,7-dioate (MW = 300)

The pyrolysis of poly(ethyl methacrylate) occurs similarly to that of poly(methyl methacrylate). The pyrogram of a sample of poly(ethyl methacrylate), CAS# 9003-42-3, with $M_w = 515,000$ is shown in Figure 6.7.31. The pyrolysis was done in identical conditions as for poly(methyl methacrylate). The peak identification for the chromatogram shown in Figure 6.7.31 was done using MS spectral library searches only and is given in Table 6.7.21.

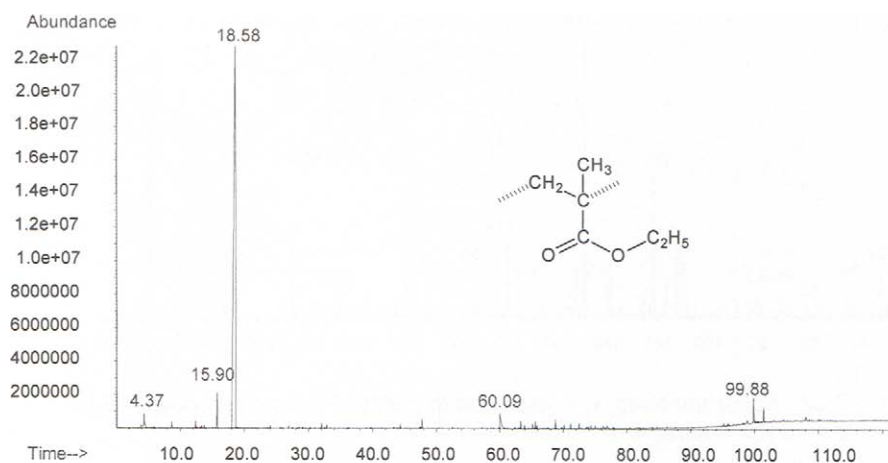


FIGURE 6.7.31. Result for a Py-GC/MS analysis of poly(ethyl methacrylate) $M_W = 515,000$. Pyrolysis done on 0.4 mg material at 600°C in He, with the separation on a Carbowax type column.

TABLE 6.7.21. Compounds identified in the pyrogram of poly(ethyl methacrylate) $M_W = 515,000$ shown in Figure 6.7.31.

Peak	Compound	Ret. Time	MW	Area %
1	carbon dioxide + ethene	4.37		2.03
2	3-methyleneheptane	8.68	112	trace
3	ethanol	12.38	46	trace
4	2-methyl-2-propenoic acid methyl ester	15.90	100	2.38
5	2-methyl-2-propenoic acid ethyl ester (monomer)	18.58	114	89.02
6	2-methylpentanoic acid ethyl ester	24.05	144	trace
7	2-methylenebutanoic acid ethyl ester	25.68	128	trace
8	2,4-dimethyl-4-pentenoic acid ethyl ester	32.06	156	trace
9	ethyl 1-cyclohexene-1-carboxylate	44.36	154	trace
10	2-ethylhexanol ?	47.81	130	0.53
11	2-methyl-2-propenoic acid	60.09	86	2.08
12	2-pentenedioic acid diethyl ester	63.29	186	0.42
13	1,2-cyclohexandicarboxylic acid diethyl ester	65.61	228	0.39
14	unknown [91(100), 118(70), 69(32), 192(18), 154(11)]	68.77	192	0.52
15	benzoic acid phenyl ester	99.88	198	1.52
16	diethyl 4-(ethoxycarbonyl)-4,6,6-trimethyl-2-methyleneheptane-1,7-dioate	101.45	342	1.10

Similar to the case of poly(methyl methacrylate), the mass spectra of some of the pyrolysate compounds are not available in common mass spectral libraries. One such example is the spectrum of diethyl 4-(ethoxycarbonyl)-4,6,6-trimethyl-2-methyleneheptane-1,7-dioate shown in Figure 6.7.32.

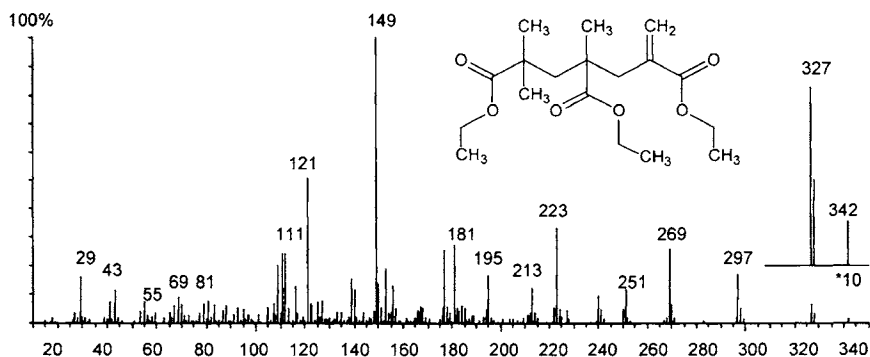


FIGURE 6.7.32. Spectrum tentatively assigned to diethyl 4-(ethoxycarbonyl)-4,6-trimethyl-2-methyleneheptane-1,7-dioate ($MW = 342$).

Two peaks from the pyrogram, namely 2-ethylhexanol and benzoic acid phenyl ester do not seem to be formed from the poly(ethyl methacrylate) pyrolysis and are probably additives. Also, 2-methyl-2-propenoic acid methyl ester identified in the pyrogram is either a contaminant or an artifact of the analysis (carryover in the GC/MS system).

Among polymethacrylate esters with various practical applications, mainly in paints and coatings, are poly(butyl methacrylates). Four different butyl groups can be used to esterify the methacrylic acid, *n*-butyl $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$, *iso*-butyl $-\text{CH}_2-\text{CH}(\text{CH}_3)_2$, *sec*-butyl $-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{CH}_3$, and *tert*-butyl $-\text{C}(\text{CH}_3)_3$. Some of the thermal decomposition products (not by flash pyrolysis) of poly(*sec*-butyl methacrylate) and poly(*tert*-butyl methacrylate) are indicated in Table 6.7.19. The results for a Py-GC/MS analysis of a sample of poly(*n*-butyl methacrylate), CAS# 9003-63-8, and of poly(*iso*-butyl methacrylate), CAS# 9011-15-8, are discussed below. The pyrogram for the sample of poly(*n*-butyl methacrylate) with $M_w = 320,000$ is shown in Figure 6.7.33. The pyrolysis was done in similar conditions to other examples, namely at 600°C in He at a heating rate of 20°C/ms with the separation on a Carbowax column (see Table 4.2.2) and MS detection. The peak identification for the chromatogram was done using MS spectral library searches only and is given in Table 6.7.22.

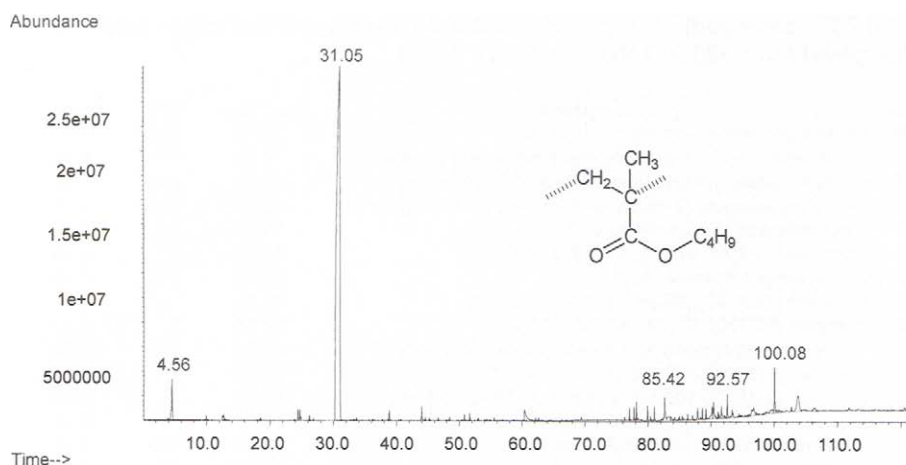


FIGURE 6.7.33. Result for a Py-GC/MS analysis of poly(*n*-butyl methacrylate) $M_W = 320,000$. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 6.7.22. Compounds identified in the pyrogram of poly(*n*-butyl methacrylate) $M_W = 320,000$ shown in Figure 6.7.33.

Peak	Compound	Ret. Time	MW	Area %
1	carbon dioxide	4.39	44	trace
2	1-butene	4.56	56	1.87
3	butanal	9.56	72	trace
4	benzene	12.48	78	0.38
5	3-buten-2-one	12.51	70	trace
6	2-methyl-2-propenoic acid methyl ester	15.96	100	trace
7	water	18.24	18	trace
8	propanoic acid butyl ester	24.20	130	trace
9	1-butanol	24.41	74	0.36
10	2-methylpropanoic acid butyl ester	24.67	144	0.56
11	2-butenic acid butyl ester	26.20	142	0.23
12	2-methyl-2-propenoic acid butyl ester (monomer)	31.05	142	82.87
13	cyclopropanecarboxylic acid 3-methylbutyl ester	33.63	156	0.12
14	2-propenyl-cyclopentane	38.81	110	0.38
15	4,4,5-trimethyl-2-hexene ?	44.00	126	0.53
17	1-methyl-1-cyclohexanecarboxylic acid ?	45.20	142	trace
18	butyl caprylate	48.42	200	0.11
19	unknown [74(100), 69(93), 130(47), 41(46), 198(14)]	50.78		0.27
20	unknown [74(100), 55(59), 69(50), 130(47), 41(46), 198(14)]	51.62		0.24
21	3,4-dimethyl-2,4-pentadienoic acid isopropyl ester ?	55.51	168	0.12
22	2-methyl-2-propenoic acid	60.29	86	0.90
23	2-methyl-2-pentenoic acid	63.20	114	0.14
24	2-methyl-2-propenoic acid ethyl ester ?	69.31	114	trace
25	methylbutanedioic acid bis(1-methylpropyl) ester ?	76.29	244	0.16
26	1,1'-biphenyl	77.01	154	0.48
27	unknown [143(100), 115(60), 199(57), 170(36)]	77.75		0.43

TABLE 6.7.22 (continued). Compounds identified in the pyrogram of poly(*n*-butyl methacrylate) $M_w = 320,000$ shown in Figure 6.7.33.

Peak	Compound	Ret. Time	MW	Area %
28	benzenepropanoic acid methylbutylester	78.14	220	0.58
29	pentanedioic acid 2,4-dimethyl-bis(1-methylpropyl) ester ?	79.91	172	0.44
30	dibutylitaconate [methylenesuccinic acid dibutyl ester]	80.98	242	0.52
31	diethyl mesaconate [2-methyl-2-butendioic acid diethyl ester]	82.20	186	0.61
32	2-butenic acid 2-propenyl ester ?	84.23	126	0.11
33	unknown [69(100), 97(33), 41(32), 211(14)]	85.02		0.24
34	2,5-dimethyl-4-hexenoic acid ?	85.42	142	0.29
35	unknown [123(100), 95(26), 151(22), 225(13)]	87.05		0.23
36	unknown [69(100), 97(33), 41(32), 211(14)]	87.85		0.43
37	cyclopentanecarboxylic acid 1-methyl-2-oxo-ethyl ester ?	88.61	170	0.38
38	unknown [199(100), 97(59), 43(15), 143(11)]	90.38		0.58
39	unknown [81(100), 109(83), 211(67), 127(54), 183(36), 155(31)]	91.08		0.60
40	unknown [69(100), 41(43), 55(40), 141(30), 140(27), 180(10)]	91.64		0.42
41	3-methylhexandioic acid dibutyl ester	92.57	272	0.90
42	benzoic acid phenyl ester	100.08	198	1.76
43	unknown [151(100), 45(36), 125(20), 115(19), 278(11), 304(1)]	103.37		1.76

The pyrogram for the sample of poly(*iso*-butyl methacrylate) with $M_w = 300,000$ is shown in Figure 6.7.34. The pyrolysis was done in similar conditions to other examples, namely at 600° C in He at a heating rate of 20° C/ms with the separation on a Carbowax column (see Table 4.2.2) and MS detection. The peak identification for the chromatogram was done using MS spectral library searches and is given in Table 6.7.23.

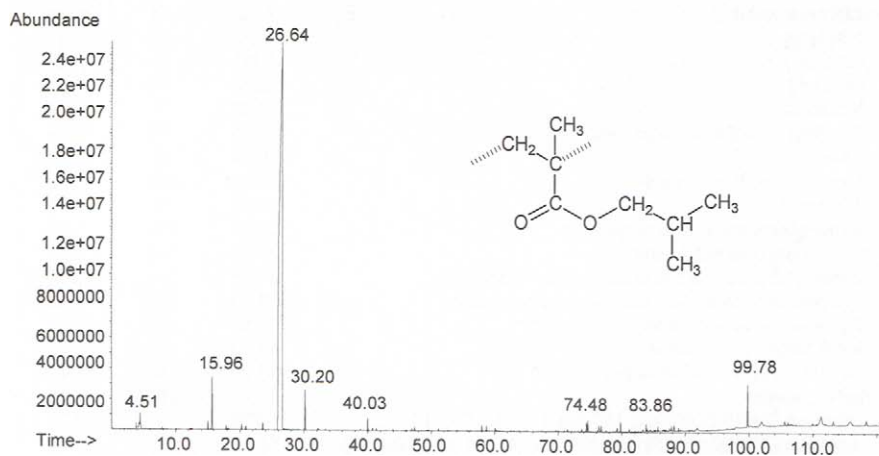


FIGURE 6.7.34. Result for a Py-GC/MS analysis of poly(*iso*-butyl methacrylate) $M_w = 300,000$. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 6.7.23. Compounds identified in the pyrogram of poly(iso-butyl methacrylate) $M_w = 300,000$ shown in Figure 6.7.34.

Peak	Compound	Ret. Time	MW	Area %
1	2-methyl-1-propene	4.51	56	0.73
2	mix 2-methylpropanal + butane	7.94		
3	benzene	12.33		trace
4	2-propenoic acid ethyl ester	15.05	100	0.32
5	2-methyl-2-propenoic acid methyl ester	15.96	100	2.16
6	methacrylic acid propyl ester	17.86	128	trace
7	propanoic acid 2-methylpropyl ester	18.30	130	trace
8	2-methylpropanoic acid 2-methylpropyl ester	20.93	144	trace
9	2-propenoic acid 2-methylpropyl ester	23.62	128	0.31
10	2-methyl-2-propenoic acid 2-methylpropyl ester (monomer)	26.64	142	90.40
11	2-methylbutanoic acid 2-methylpropyl ester	26.85	158	0.74
12	2-methyl-2-propenoic acid butyl ester	30.20	142	1.50
13	2-methyl-2-propenoic acid 2-methoxyranyl ester ?	32.17	142	trace
14	2,4-dimethyl decene ?	40.03	168	0.44
15	diisobutyl itaconate	74.48	242	0.37
16	α -methylbenzenepropanoic acid ?	74.70	164	0.44
17	2-methyl-2-propenoic acid 1,2-ethandiyl ester	79.86	198	0.40
18	2-butenic acid 2-propenylidene ester	83.87	210	0.25
19	benzoic acid phenyl ester	99.78	198	1.93

Similar to the case of other poly(butyl acrylates), the pyrogram of poly(isobutyl methacrylate) shows small amounts of poly(methyl methacrylate). This is the result of an impurity in the polymer, and it is not due to the side chain fragmentation.

Analytical pyrolysis results for one more polymethacrylate is given in Figure 6.7.35. The substance analyzed is poly(lauryl methacrylate), CAS# 25719-52-2, $M_w = 470,000$ with the idealized formula $(-\text{CH}_2\text{C}(\text{CH}_3)[\text{COO}(\text{CH}_2)_{11}\text{CH}_3]-)_n$. The pyrolysis was done in similar conditions to other examples in this book (see Table 4.2.2) and MS detection.

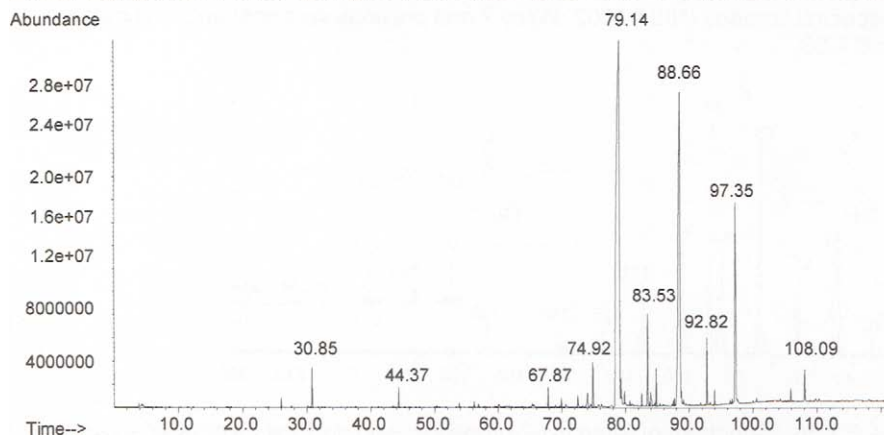


FIGURE 6.7.35. Result for a Py-GC/MS analysis of poly(lauryl methacrylate), $M_w = 470,000$. Sample not pure, containing various proportions of poly(tridecyl methacrylate), poly(tetradecyl methacrylate), poly(pentadecyl methacrylate), and poly(hexadecyl methacrylate). Pyrolysis done on 0.4 mg material at 600°C in He, with the separation on a Carbowax type column.

The peak identification for the chromatogram was done using MS spectral library searches and is given in Table 6.7.24. The peak identification showed that this polymer was not a pure poly(dodecyl methacrylate) (monomer eluting at 79.14 min.) and also contains various proportions of poly(tridecyl methacrylate) (monomer eluting at 83.53 min.), poly(tetradecyl methacrylate) (monomer eluting at 88.66 min.), poly(pentadecyl methacrylate) (monomer eluting at 92.82 min.), and poly(hexadecyl methacrylate) (monomer eluting at 97.35 min.).

TABLE 6.7.24. Compounds identified in the pyrogram of poly(lauryl methacrylate) (sample not pure), $M_w = 470,000$, shown in Figure 6.7.35.

Peak	Compound	Ret. Time	MW	Area %
1	2-butenic acid butyl ester	26.20	142	0.21
2	1-dodecene	30.85	168	0.92
3	1-tetradecene	44.37	196	0.46
4	2-methyl-2-propenoic acid hexyl ester	56.23	170	0.13
5	2-methyl-2-propenoic acid	60.29	86	trace
6	2-methyl-2-propenoic acid octyl ester	67.87	198	0.49
7	2-methyl-2-propenoic acid decyl ester	72.55	226	0.43
8	propanoic acid decyl ester	74.07	214	0.67
9	1-dodecanol	74.92	186	1.17
10	2-methyl-2-propenoic acid dodecyl ester	79.14	254	51.05
11	2-methyl-2-propenoic acid tridecyl ester	83.53	268	2.75
12	1-tetradecanol	84.87	214	0.93
13	2-methyl-2-propenoic acid tetradecyl ester	88.66	282	28.37
14	2-methyl-2-propenoic acid pentadecyl ester	92.82	296	1.74
15	1-hexadecanol	94.02	242	0.36
16	2-methyl-2-propenoic acid hexadecyl ester	97.35	310	9.29
17	unknown [69(100), 155(39), 87(25), 41(22), ...173(9)]	108.09		1.04

The spectrum of 2-methyl-2-propenoic acid dodecyl ester is available in commercial mass spectral libraries (NIST 2002, Wiley 7 and previous versions) and is shown in Figure 6.7.36.

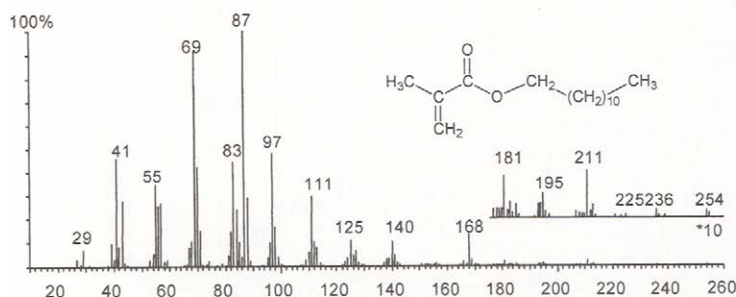


FIGURE 6.7.36. Spectrum of 2-methyl-2-propenoic acid dodecyl ester ($MW = 254$) available in commercial mass spectral libraries.

The spectra of 2-methyl-2-propenoic acid tridecyl, tetradecyl, pentadecyl and hexadecyl ester are not available in common commercial libraries. The spectrum assignment for

each of these compounds eluting at 83.53 min., 88.66 min., 92.82 min. and 97.35 min., respectively, was done based on the similarity with the spectrum of 2-methyl-2-propenoic acid dodecyl ester and the detection of the molecular ion. These spectra are shown in Figures 6.7.37 to 6.7.40.

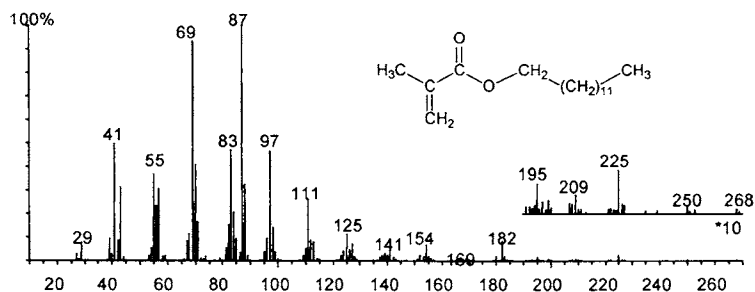


FIGURE 6.7.37. Spectrum of 2-methyl-2-propenoic acid tridecyl ester (MW = 268).

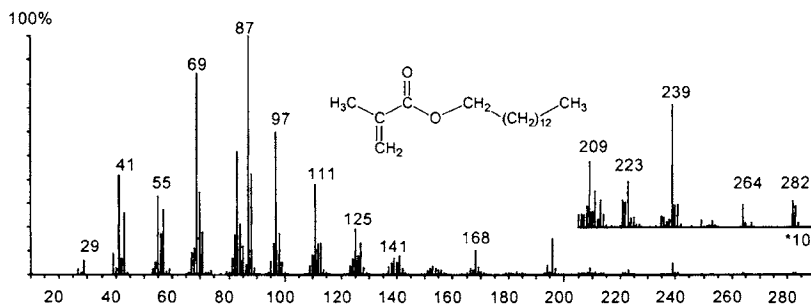


FIGURE 6.7.38. Spectrum of 2-methyl-2-propenoic acid tetradecyl ester (MW = 282).

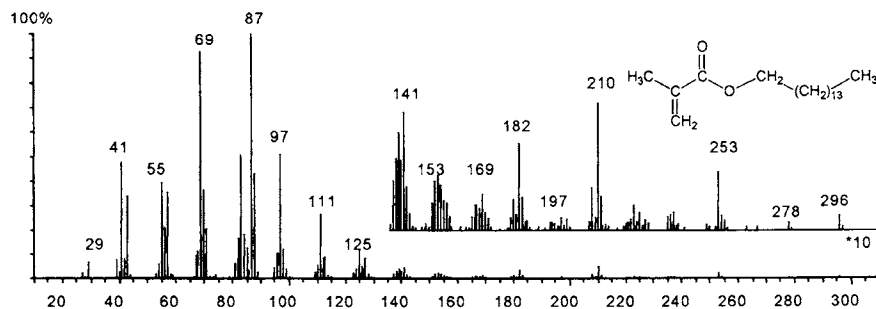


FIGURE 6.7.39. Spectrum of 2-methyl-2-propenoic acid pentadecyl ester (MW = 296).

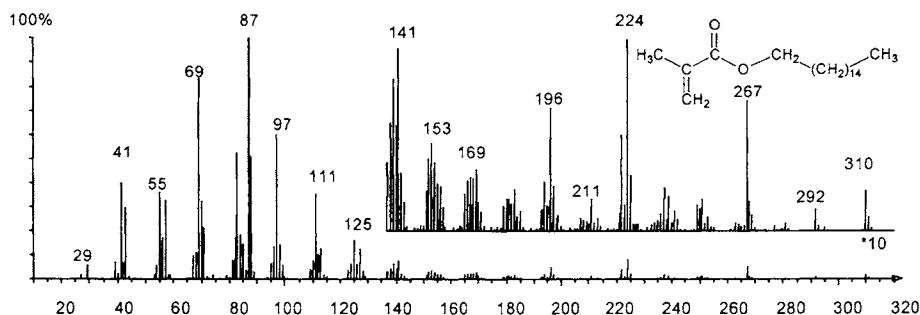


FIGURE 6.7.40. Spectrum of 2-methyl-2-propenoic acid hexadecyl ester (MW = 310)

As seen from the previous examples, poly(methacrylic acid esters) generate a significant amount of monomer. Small amounts of compounds derived from two monomer or even three monomer units can be seen in some pyrograms (when the elution from the selected chromatographic column is feasible). However, the use of Py-GC/MS for polymer identification can be based mainly on the presence of the monomer. Some difficulty may arise in differentiating esters with isomeric alcohol component such as poly(*n*-butyl methacrylate) and poly(*iso*-butyl methacrylate), since 2-methyl-2-propenoic acid *n*-butyl ester and 2-methyl-2-propenoic acid 2-methylpropyl ester have very similar mass spectra.

Among other poly(methacrylate esters), hydroxyalkyl methacrylates play an important role in practice. Due to their hydrophilic character they have important biomedical applications (transdermal drug delivery systems, contact lenses) and can be used in copolymers for improving wettability and dyeing properties of fibers. The result for flash pyrolysis, using Py-GC/MS analysis of a sample of poly(2-hydroxyethyl methacrylate), CAS# 25249-16-5, with $M_w = 20,000$ is shown in Figure 6.7.41. The polymer has the idealized structure $[-CH_2C(CH_3)(COOCH_2CH_2OH)-]_n$. The pyrolysis was done in similar conditions to other examples, namely at 600° C in He at a heating rate of 20° C/ms with the separation on a Carbowax column (see Table 4.2.2) and MS detection. The peak identification for the chromatogram shown in Figure 6.7.27 was done using MS spectral library searches and is given in Table 6.7.25.

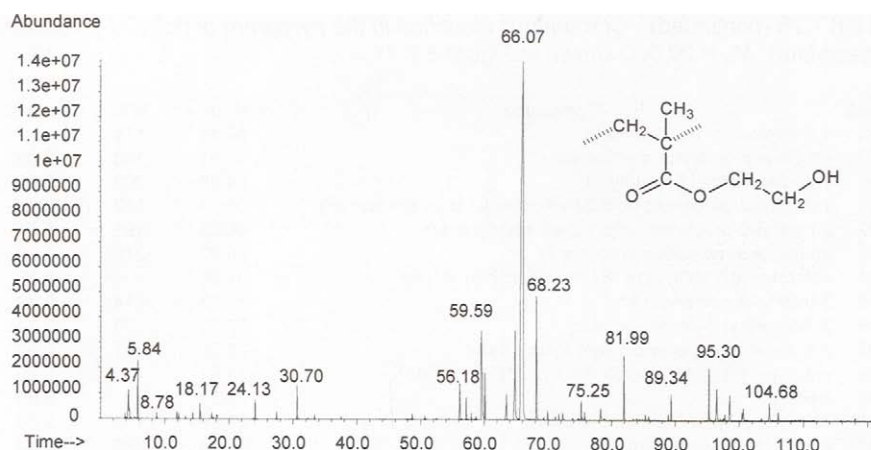


FIGURE 6.7.41. Result for a Py-GC/MS analysis of poly(2-hydroxyethyl methacrylate), $M_w = 20,000$. Pyrolysis done on 0.4 mg material at 600°C in He, with the separation on a Carbowax type column.

TABLE 6.7.25. Compounds identified in the pyrogram of poly(2-hydroxyethyl methacrylate), $M_w = 20,000$ shown in Figure 6.7.41.

Peak	Compound	Ret. time	MW	Area %
1	carbon dioxide	4.37	44	1.86
2	2-methylpropene	4.52	56	0.58
3	acetaldehyde	5.84	44	2.08
4	2-propenal	8.78	56	0.19
5	2-propanol	11.91	60	0.35
6	ethanol	12.21	46	0.28
7	3-hexanone	13.26	100	0.09
8	2-methyl-2-propenenitrile (impurity from initiator)	14.41	67	0.21
9	2-methylpropanenitrile (impurity from initiator)	15.52	69	0.61
10	2-methyl-2-propenoic acid methyl ester	15.96	100	0.00
11	2-methyl-2-propenoic acid ethenyl ester	17.37	112	0.21
12	2,2-dimethyl-3-heptanone ?	17.62	142	0.00
13	2-methyl-2-propenoic acid ethyl ester	18.11	114	0.15
14	water	18.17	18	0.18
15	undecene	23.86	154	0.00
16	1,3-dimethylcyclopentane	24.13	98	0.64
17	dodecane	27.48	170	0.20
18	1-dodecene	30.70	168	1.10
19	unknown [55(100), 108(24), 123(20), 39(14), 81(10)]	33.39		0.13
20	1-tridecene	37.53	182	0.00
21	2-ethoxyethyl methacrylate	48.69	158	0.20
22	propanoic acid	50.64	74	0.16
23	1,2-ethanediol	56.18	62	1.87
24	2,2'-azobis(2-methylpropanenitrile) (AIBN initiator)	57.19	98	0.84
25	2,2-dimethylpropanoic acid ethyl ester ?	57.97	158	0.19
26	2-methylbutanoic acid	58.70	102	0.14
27	2-methyl-2-propenoic acid	59.59	86	6.05

TABLE 6.7.25 (continued). Compounds identified in the pyrogram of poly(2-hydroxyethyl methacrylate), $M_w = 20,000$ shown in Figure 6.7.41.

Peak	Compound	Ret. time	MW	Area %
28	1,2-ethanediol dipropanoate	60.14	174	1.67
29	ethylene propionate methacrylate	63.51	186	0.00
30	1-dodecanethiol (impurity ?)	64.85	202	5.65
31	2-methyl-2-propenoic acid 2-hydroxyethyl ester (monomer)	66.07	112	55.06
32	2-methyl-2-propenoic acid 1,2-ethanediyl ester	68.23	198	5.54
33	dodecylmethyl sulfide (impurity ?)	69.37	216	0.10
34	unknown [87(100), 200(18), 129(9), 157(8), 41(5)]	69.95		0.35
35	2-methyl-4-pentenoic acid	71.75	114	0.22
36	2,2-dimethyl-3-pentenoic acid	72.35	128	0.34
37	2,4-dimethyl-4-pentenoic acid methyl ester	75.25	142	0.83
38	unknown [97(100), 55(25), 69(16), 81(11), 419(10)]	75.81		0.30
39	mixture	78.31		0.65
40	diethyleneglycol monomethacrylate	81.99	174	2.50
41	ester of triethylene glycol	89.34	286	0.94
42	unknown	95.31		1.81
43	unknown	96.49		1.65
44	unknown	98.52		0.97
45	4-propylcyclohexanecarboxylic acid 4-ethoxyphenyl ester ?	100.46	290	0.79
46	unknown [83(100), 111(93), 82(86), 110(74), 55(57)]	100.63		0.97
47	unknown [136(100), 99(38), 81(23), 85(22), 68(14)]	104.68		0.79
48	unknown [201(100), 215(24), 55(27), 246(37), 61(24)]	106.07		0.60

Pyrolysis process for poly(2-hydroxyethyl methacrylate) occurs similarly to that for other methacrylic acid esters. The formation of 2-methyl-2-propenoic acid 2-hydroxyethyl ester, the monomer, shows that unzipping is a significant part of the process. Some other compounds in the pyrolysate also are generated from the polymer cleavage, such compounds including 2-methyl-2-propenoic acid ethenyl ester, propanoic acid, 2-methyl-2-propenoic acid, ethanol, etc. On the other hand, some compounds are not expected in the pyrolysate and they can be impurities or additives. Examples of such compounds are the hydrocarbons (undecene, dodecane, 1-dodecene, etc.), the esters of ethylene diol and the free 1,2-ethandiol, etc. The initiator AIBN and its decomposition products 2-methyl-2-propenenitrile and 2-methylpropanenitrile identified in the pyrolysate show that the polymer was obtained using AIBN as initiator.

- Other poly(methacrylic acid derivatives)

Thermal stability of some other poly(methacrylic acid derivatives) are reported in literature. Some of these reports are summarized in Table 6.7.26 [6].

TABLE 6.7.26. Summary regarding literature reports on thermal decomposition of other poly(methacrylic acid derivatives).

Polymer	Temp. °C	Results	Ref.
poly(methacrylamide)	up to 340	NH ₃ and H ₂ O	165
poly(methacrylamide)	above 340	chain fragments (50%) in which a high proportion of amide groups have been converted to cyclic imides; small amounts of CO ₂ , CH ₄ , HCN	165
poly(methacrylamide)	ambient to 500	NH ₃ , HCN, isobutene, CO ₂ (trace), methacrylonitrile (trace)	120
poly(methacrylonitrile)	<200	nonvolatile materials	166
poly(methacrylonitrile)	220–270	50–100% monomer depending upon pretreatment and purity of the polymer	166
poly(methacrylonitrile)	ambient to 500	ethene, propene, isobutene, HCN, CO ₂ (from benzoyl peroxide end groups), methacrylonitrile (major product), 2-cyanobutane, 2-cyanopentene, CH ₄	167

In general, pyrolysis of poly(methacrylic acid derivatives) have a thermal behavior similar to those of the corresponding poly(acrylic acid derivatives). However, the amount of monomer is typically higher for the methacrylic series.

- Copolymers of methyl and other esters of methacrylic acid

Methacrylates are used frequently in copolymers. For classification purposes these copolymers can be included in several groups. One group consists of copolymers between two different methacrylate esters. Their properties are not very different from that of the main homopolymer methacrylate. Examples of copolymers from this group are poly(methyl methacrylate-co-ethyl methacrylate), poly(methyl methacrylate-co-butyl methacrylate), poly(methyl methacrylate-co-dodecyl methacrylate), poly(methyl methacrylate-co-*tert*-butylphenyl methacrylate), poly(butyl methacrylate-co-isobutyl methacrylate), poly(lauryl methacrylate-co-glycidyl methacrylate), poly(methyl methacrylate-co-ethyl acrylate) with uses in adhesives, coatings, paints, and as binders in inks. Another group is that of hydroxyethylmethacrylate with other comonomers such as acrylic acid, methacrylic acid, methyl methacrylate, styrene, etc. Due to the hydrophilic properties of hydroxyethyl groups, these copolymers have important biomedical uses for transdermal delivery systems and contact lenses and in copolymers used as fibers for increasing wettability and improved capability for dyeing. Alkyl methacrylates also form copolymers with olefins such as ethene, butadiene, chloroprene, vinylidene chloride, and tetrafluoroethylene. These copolymers are used as viscosity modifiers in mineral oils (when their DP is not very high) or as multi-purpose thermoplastic materials with good mechanical resistance. Other copolymers are used as multi-purpose thermoplastic materials or in fibers. In this group can be included poly(methyl methacrylate-co-acrylonitrile), poly(methyl methacrylate-co-acrylonitrile-co- α -methylstyrene), poly(methyl methacrylate-co-butadiene-co-styrene), and poly(methyl methacrylate-co-acrylonitrile-co-butadiene-co-styrene). Poly(alkyl methacrylates-co-styrene), where alkyl can be methyl, ethyl, butyl, isobutyl, hexyl, octyl, etc., are added to homopolymer blends to improve interphase adhesion leading to better mechanical properties. A variety of other copolymers with different properties include poly(methyl methacrylate-co-N-vinylpyrrolidone), poly(methyl methacrylate-co-vinyl alcohol), poly(ethyl methacrylate-co-acrylamide), and poly(butyl methacrylate-co-

methacrylamide). More complicated copolymers also are known, such as methacrylate/urethane copolymers where various urethanes are copolymerized with methyl methacrylate, such as hexamethane diisocyanate/tetraethylene glycol/hydroxyethyl methacrylate copolymer with methyl methacrylate. Besides copolymers, methacrylates are used in various blends with polybutadiene, polycarbonates, poly(ethylene oxide), poly(vinyl chloride), poly(vinylidene fluoride), etc.

Some results on pyrolysis or thermal decomposition of copolymers of methacrylic acid esters are reported in literature [59, 100, 168–180], etc. Some other reports are summarized in Table 6.7.27 [6].

TABLE 6.7.27. Summary regarding literature information on thermal decomposition of several copolymers of methacrylic acid esters.

Polymer	Temp. °C	Results	Ref.
hydroxyethyl methacrylate-co-methacrylic acid	402–407	60% weight loss by unzipping process	181
poly(methyl methacrylate)-blend-ammonium polyphosphate	ambient to 450	H ₂ O and NH ₃ from ammonium polyphosphate; methyl methacrylate (major product), CO, CO ₂ , methanol, dimethyl ether, hydrocarbons, high boiling chain fragments	182
poly(methyl methacrylate)-blend-poly(vinyl acetate) 10/1-1/1 w/w	ambient to 500	methyl methacrylate, acetic acid, methyl acetate, methanol, CO ₂ , butene, benzene, ketene	183
poly(methyl methacrylate)-blend-poly(vinyl bromide) 50/50 mol/mol	ambient to 500	methyl methacrylate, HBr, CO, CO ₂ , and other unidentified products	184
poly(methyl methacrylate-co-2,2,2-trichloroethyl-methacrylate) 24% TCMA	600	CO ₂ , propene, vinyl chloride, vinylidene chloride, dichloroacetaldehyde, methyl methacrylate	39
poly(methyl methacrylate-co-2,3-dibromopropyl-methacrylate) 16 mol% DBPMA	600	CO, CO ₂ , ethene, propene, methyl bromide, butene, vinyl bromide, ethyl bromide, 1-bromopropene, 2-bromopropene, cyclopropyl bromide, methyl methacrylate	34
poly(methyl methacrylate-co-2-bromoethyl methacrylate)	ambient to 500	methyl methacrylate, 2-bromoethyl methacrylate, traces of vinyl bromide and CO ₂	149
poly(methyl methacrylate-co-2-bromoethyl-methacrylate) 22 mol% BEMA	600	CO ₂ , propene, acetaldehyde, methyl bromide, butene, vinyl bromide, methyl methacrylate	34
poly(methyl methacrylate-co-2-chloroethyl-methacrylate) 22 mol% CEMA	600	CO ₂ , propene, acetaldehyde, vinyl chloride, ethyl chloride, methyl methacrylate	36
poly(methyl methacrylate-co-2-ethylhexylacrylate)	750	methyl methacrylate, 2-ethylhexylacrylate, 2-ethyl-1-hexene	185
poly(methyl methacrylate-co-2-sulfoethyl methacrylate) 20, 40, 60 mol% MMA	50–600	CO, CO ₂ , H ₂ O, SO ₂ , ethene, methanol, methyl methacrylate (only 60 and 80 mol% methyl methacrylate copolymers)	150
poly(methyl methacrylate-co-4-vinylpyridine) 22, 35, 46, 56 mol% VP	ambient to 500	4-vinyl pyridine, methyl methacrylate, traces of pyridine and 4-methyl pyridine	186
poly(methyl methacrylate-co-acrylonitrile-co-butadiene-co-styrene)	260	thermally stable	187
poly(methyl methacrylate-co-diallyl phthalate)	750	methyl methacrylate, prop-2-enyl benzoate, benzoic acid, phthalic anhydride, di(prop-2-enyl) phthalate	100

TABLE 6.7.27 (continued). Summary regarding literature information on thermal decomposition of several copolymers of methacrylic acid esters.

Polymer	Temp. °C	Results	Ref.
poly(methyl methacrylate-co-glycidyl methacrylate)	ambient to 500	CH ₄ , CO, CO ₂ , propene, isobutene, dimethyl ketene, acrolein, allyl alcohol, glycidol, glycidyl methyl ether, methyl methacrylate, glycidyl methacrylate, chain fragments; distribution varies with copolymer composition	188
poly(methyl methacrylate-co-isobornyl methacrylate)	750	methyl methacrylate, isobornyl methacrylate, camphene, camphene isomers	185
poly(methyl methacrylate-co-methacrylamide)	up to 340	less than 35 mol% methacrylamide. MMA, methanol, NH ₃ , H ₂ O	165
poly(methyl methacrylate-co-methacrylamide)	>340	methacrylamide; chain fragments and small amounts of CH ₄ , CO ₂ , CO, HCN, methacrylonitrile and isobutene	165
poly(methyl methacrylate-co-methacrylamide)	-	less than 10 mol% methacrylamide, degradation becomes progressively more like that of PMMA	165
poly(methyl methacrylate-co-methacrylamide)	-	initial decomposition 220° C for 61% MMA, 230° C for 55% MMA, 237° C for 48% MMA	189, 190
poly(methyl methacrylate-co-methacrylic acid Li, Na, K salt) 0–100 mol%	ambient to 500	CO ₂ , alkenes, CH ₄ , CO, propanal, methanol (major), acetone, 2-methylpropanal, methacrolein, butanal, methyl ethyl ketone, methyl isopropyl ketone, methyl isopropenyl ketone, methyl methacrylate (major), methyl prop-2-enyl ketone, toluene, di-isopropyl ketone, cyclopentanone, 2-methyl cyclopentanone, 2,5-dimethyl cyclopentanone, 2,5-di-methylcyclopent-3-enone. Relative yields depend upon salt and copolymer composition	191
poly(methyl methacrylate-co-methacrylic acid)	<300	H ₂ O and methanol	192
poly(methyl methacrylate-co-methacrylic acid)	>300	methyl methacrylate, CO ₂ , CO, CH ₄	192
poly(methyl methacrylate-co-methacrylic acid)	900	(50/50 and 75/25); CO ₂ , propene, butenes, pentenes, pentadienes, hexene, hexadienes, hexatrienes, benzene, methyl isobutyrate, methyl methacrylate, toluene, heptene, heptatriene, methylpentenoate, methacrylic acid, xylene, octatriene, octadiene, nonatriene, hexadienoic acid, decatriene, decatetraene, decapentaene, undecatriene, methylbenzoic acids	125
poly(methyl methacrylate-co-methyl- α -bromoacrylate) 22 mol% MBA	600	CO ₂ , acetaldehyde, methyl bromide, butene, vinyl bromide, unidentified alkenyl bromides, methyl methacrylate	34
poly(methyl methacrylate-co-methyl- α -chloroacrylate) 38 mol% MCA	600	CO ₂ , propene, methyl chloride, methyl methacrylate	36
poly(methyl methacrylate-co-n-butyl methacrylate)	750	ethylene, CO ₂ , propene, but-1-ene, methyl methacrylate, n-butyl methacrylate	185
poly(methyl methacrylate-co-phenyl methacrylate) 9, 18, 47, 88 mol% PMA	ambient to 500	CO ₂ , isobutene, ketene, formaldehyde, methanol, methyl methacrylate, phenyl methacrylate, chain fragments including six-membered anhydride ring structures. Product distribution varies with copolymer composition with non-monomer products most pronounced at low PMA contents	161
poly(methyl methacrylate-co-vinyl acetate) 5–40 mol% VA	ambient to 500	acetic acid, methyl methacrylate, methyl acetate, chain fragment fraction, ketene, CO ₂	193
poly(methyl methacrylate-co-vinyl bromide) 6–75 mol% VB	ambient to 500	methyl methacrylate, methyl bromide, methanol, CO ₂ , methanol, HBr, CO, H ₂ , other unidentified minor products, relative amounts depend upon copolymer composition	184

The results for a Py-GC/MS analysis of a poly(butyl methacrylate-co-methyl methacrylate), monomer ratio methyl/butyl 0.7/1.0, sample are shown in Figure 6.7.42. The polymer has the CAS# 25608-33-7, $M_w = 100,000$ and the idealized formula

$[\text{CH}_2\text{C}(\text{CH}_3)(\text{COOCH}_3)]_x [\text{CH}_2\text{C}(\text{CH}_3)(\text{COOC}_4\text{H}_9)]_y$. The pyrolysis was done at 600°C in He at a heating rate of $20^\circ\text{C}/\text{msec}$ with 10 sec. THT. The separation conditions were the same as for other examples previously discussed (see Table 4.2.2). The peak identification for the chromatogram shown in Figure 6.7.42 was done using MS spectral library searches only and is given in Table 6.7.28.

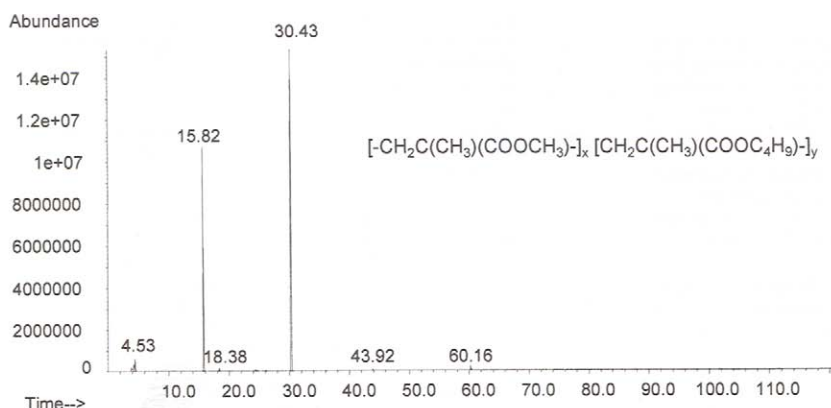


FIGURE 6.7.42. Result for a Py-GC/MS analysis of poly(butyl methacrylate-co-methyl methacrylate), monomer mole ratio methyl/butyl 0.7/1.0, $M_w = 100,000$. Pyrolysis done on 0.4 mg material at 600°C in He, with the separation on a Carbowax type column.

TABLE 6.7.28. Compounds identified in the pyrogram of poly(butyl methacrylate-co-methyl methacrylate), monomer mole ratio methyl/butyl 0.7/1.0, $M_w = 100,000$, as shown in Figure 6.7.42.

Peak	Compound	Ret. Time	MW	Area %
1	carbon dioxide	4.35	44	1.17
2	2-methylpropene	4.53	56	1.67
3	2-methyl-2-propenoic acid methyl ester (monomer)	15.82	100	28.14
4	water	18.38	18	0.51
5	propanoic acid butyl ester	24.36	130	trace
6	1-butanol	24.61	74	trace
7	2-methylpropanoic acid butyl ester	24.72	144	trace
8	2-butenic acid butyl ester	26.14	142	trace
9	2-methyl-2-propenoic acid butyl ester (monomer)	30.43	142	67.53
10	2,4-dimethyl-4-pentenoic acid methyl ester ?	43.92	142	trace
11	2-methyl-2-propenoic acid	60.16	86	0.98

As seen from Figure 6.7.42 and Table 6.7.28, the main process during the pyrolysis of this copolymer is the unzipping. Mainly the two comonomers are generated in the pyrogram. The mole ratio of 2-methyl-2-propenoic acid methyl ester vs. 2-methyl-2-propenoic acid butyl ester is about 0.6/1.0, which is not very different from the expected values but slightly skewed toward the butyl ester monomer.

The copolymer poly(butyl methacrylate-co-methyl methacrylate) with a different monomer ratio methyl/butyl, namely 5.6/1.0, gives a pyrogram with a higher peak for 2-methyl-2-propenoic acid methyl ester than for 2-methyl-2-propenoic acid butyl ester, as

expected. The pyrogram is shown in Figure 6.7.43, and it was obtained in the same conditions as that shown in Figure 6.7.42. The copolymer has the same CAS# 25608-33-7 and $M_w = 75,000$. The peak identifications were obtained using MS spectral library searches only and are given in Table 6.7.29.

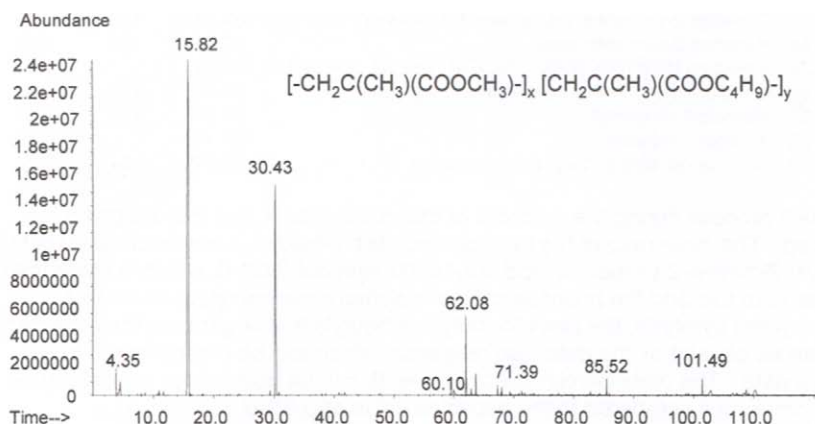


FIGURE 6.7.43. Result for a Py-GC/MS analysis of poly(butyl methacrylate-co-methyl methacrylate), monomer mole ratio methyl/butyl 5.6/1.0, $M_w = 75,000$. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 6.7.29. Compounds identified in the pyrogram of poly(butyl methacrylate-co-methyl methacrylate), monomer mole ratio methyl/butyl 5.6/1.0, $M_w = 75,000$, as shown in Figure 6.7.43.

Peak	Compound	Ret. time	MW	Area %
1	carbon dioxide	4.35	44	trace
2	2-methylpropene	4.53	56	1.67
3	propanal	7.40	58	trace
4	propanone	8.03	58	trace
5	3-methyleneheptane	8.68	112	0.15
6	methanol	10.69	32	trace
7	propanoic acid methyl ester	11.00	88	0.25
8	2-methylpropanoic acid methyl ester	11.72	102	0.23
9	2-methyl-2-propenoic acid methyl ester (comonomer)	15.82	100	57.78
10	2-propenol	22.20	58	trace
11	3-methyl-3-butenic acid methyl ester	22.75	114	trace
12	propanoic acid butyl ester	24.22	130	trace
13	2,4-dimethyl-4-pentenoic acid methyl ester	29.36	142	0.28
14	2-methyl-2-propenoic acid butyl ester (comonomer)	30.43	142	27.43
15	acetic acid 2-ethylhexyl ester	40.80	172	0.19
16	2-propenoic acid 6-methylheptyl ester	47.41	184	trace
17	2-ethyl-1-hexanol	47.71	130	trace
18	2,4-dimethyl-pentanedioic acid dimethyl ester	56.64	188	trace
19	methylenebutanedioic acid dimethyl ester	59.56	158	0.30
20	2-methyl-2-propenoic acid	60.10	86	0.79
21	2-methyl-2-propenoic acid 2-hydroxypropyl ester	62.08	144	5.18
22	2-methyl-3-methylenehexanedioic acid dimethyl ester	62.92	200	0.42

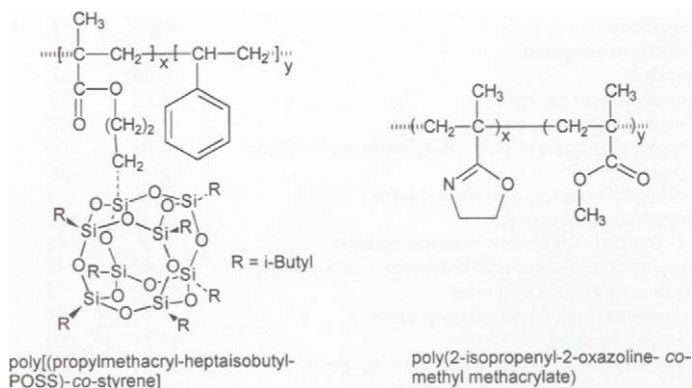
TABLE 6.7.29 (continued). *Compounds identified in the pyrogram of poly(butyl methacrylate-co-methyl methacrylate), monomer mole ratio methyl/butyl 5.6/1.0, $M_w = 75,000$, as shown in Figure 6.7.43.*

Peak	Compound	Ret. time	MW	Area %
23	2-methyl-2-propenoic acid ethanediol (di)ester	63.70	198	1.19
24	4-methyl-2-pentenoic acid	67.33	114	0.51
25	unknown [123(100), 95(98), 127(70), 126(67), 154(64)]	68.03		0.59
26	2,5-dimethyl-2-hexenedioic acid dimethyl ester	69.40	200	0.37
27	docosane (impurity)	85.52	310	0.91
28	phthalate impurity	101.49		1.11
29	dodecanoic acid undecyl ester (impurity)	108.76	354	0.64

The main process during the pyrolysis of this copolymer is also the unzipping, as expected. The mole ratio of the two comonomers 2-methyl-2-propenoic acid methyl ester vs. 2-methyl-2-propenoic acid butyl ester is about 3.0/1.0, which is lower than expected. In this and the previous case of poly(butyl methacrylate-co-methyl methacrylate) pyrolysis, the peak for butyl methacrylate is larger than the expected. This can be caused by the detection response, which can be higher for the butyl methacrylate. The other pyrolysate components cannot account for the difference in the comonomer ratio compared to the expected value of 5.6/1.0.

The comparison of the nature of compounds in the pyrolysate of the sample methyl/butyl mole ratio 0.7/1.0 with the one 5.6/1.0 shows that the second sample generated more fragments and also has some impurities. It is likely that the polymer with 5.6/1.0 methyl/butyl mole ratio was less pure compared to the other copolymer.

The results for two other polymers analyzed by Py-GC/MS are given below. One of these polymers is poly[(propylmethacryl-heptaisobutyl-POSS)-co-styrene] 25 wt % POSS, where POSS is pentacyclo[9.5.1.1(3,9).1(5,15).1(7,13)]-octasiloxane. The other is poly(2-isopropenyl-2-oxazoline-co-methyl methacrylate), CAS# 27341-60-2 and $M_w = 40,000$. The idealized structures of the two polymers are shown below:



Pyrolysis of both polymers was done at 600° C in He in similar conditions applied for other examples previously discussed (see also Table 4.2.2). The pyrogram for poly[(propylmethacryl-heptaisobutyl-POSS)-co-styrene] is shown in Figure 6.7.44, and

the peak identification was done using MS spectral library searches only and is given in Table 6.7.30.

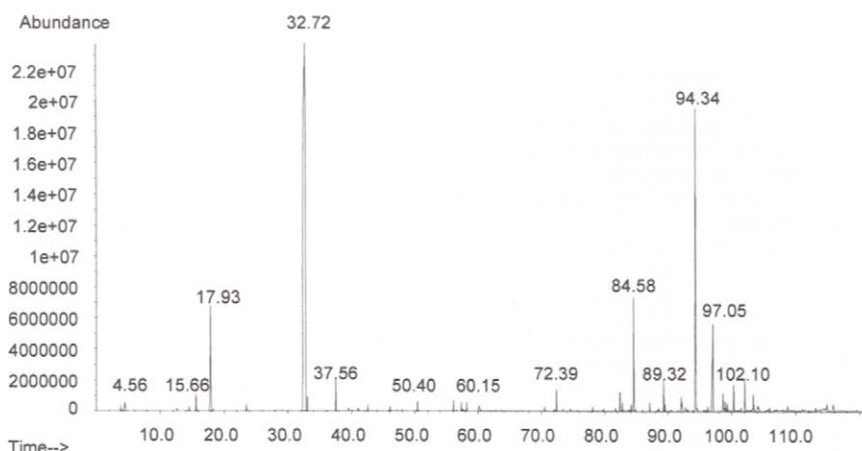


FIGURE 6.7.44. Result for a Py-GC/MS analysis of poly[(propylmethacryl-heptaisobutyl-POSS)-co-styrene] 25 wt % POSS. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 6.7.30. Compounds identified in the pyrogram of poly[(propylmethacryl-heptaisobutyl-POSS)-co-styrene] 25 wt % POSS, as shown in Figure 6.7.44.

Peak	Compound	Ret. time	MW	Area%
1	1-propene	4.56	56	0.48
2	tetrahydrofuran	9.44	72	trace
3	benzene	12.63	78	trace
4	2-methyl-2-propenenitrile	14.57	67	trace
5	2-methylpropanenitrile	15.66	69	0.69
6	toluene	17.93	92	5.74
7	ethylbenzene	23.49	106	0.27
8	propylbenzene	29.13	120	trace
9	styrene	32.77	104	51.02
10	1-propenylbenzene	33.09	118	0.55
11	α -methylstyrene (1-methylethenyl)benzene	37.56	118	1.28
12	3-butenyl benzene	39.54	132	trace
13	(1-methylenepropyl)benzene	40.98	132	trace
14	2-propenylbenzene	42.56	118	0.29
15	(3-methyl-3-butenyl)benzene	46.17	146	trace
16	(3-methyl-1-methylenebutyl)benzene	47.20	160	trace
17	1H-indene	47.99	118	trace
18	benzaldehyde	50.40	106	0.44
19	acetic acid 2-phenylethyl ester	52.82	164	trace
20	1-phenylbicyclo[2.1.1]hexane	55.01	158	trace
21	phenyloxirane	56.12	120	0.49
22	1,2-dihydronaphthalene	56.56	130	trace
23	2,2'-azobis(2-methylpropanenitrile) (AIBN)	57.35	136	0.38
24	benzeneacetaldehyde	57.66	120	trace
25	1-phenylethanone	58.23	120	0.38

TABLE 6.7.30 (continued). *Compounds identified in the pyrogram of poly[(propylmethacryl-heptaisobutyl-POSS)-co-styrene] 25 wt % POSS, as shown in Figure 6.7.44.*

Peak	Compound	Ret. time	MW	Area%
26	2-methyl-2-propenoic acid	60.12	86	0.59
27	1,3-dimethyl-1H-indene	62.78	144	trace
28	α -methylenebenzeneacetonitrile	70.36	129	trace
29	2,6-bis(1,1-dimethylethyl)-4-methylphenol (BHT)	72.03	220	trace
30	benzenepentanenitrile	72.39	159	0.93
31	1,1'-(1-methyl-1,2-ethanediyl)bisbenzene	81.71	196	trace
32	bibenzyl	82.43	182	0.86
33	1,1'-ethenylidenebisbenzene	82.80	180	0.37
34	1,1'-cyclopropylidenebisbenzene	84.20	194	0.33
35	unknown [117(100), 115(80), 118(58), 185(53), 91(26)]	84.59		4.70
36	1,1'-(1-butene-1,4-diyl)bisbenzene	87.13	208	0.42
37	2-phenyl-2,3-dihydroindene	88.39	194	trace
38	1,1'-(1,3-propandiyl)bisbenzene	89.33	196	1.32
39	1,1'-[1-(2-propenyl)-1,2-ethanediyl]bisbenzene	89.54	222	0.38
40	1,3-dimethyl-3-butenylbenzene	92.06	160	0.56
41	bicyclo[4.2.1]nona-2,4,7-triene-7-phenyl ?	92.19	194	0.40
42	(3-phenylbut-3-enyl)benzene or styrene dimer	94.36	208	15.55
43	unknown (see Figure 5.7.45)	97.08		5.39
44	1,1'-cyclopropylidenebisbenzene	98.68	194	0.94
45	1-(4-methylphenyl)-4-phenylbuta-1,3-diene	99.01	220	0.42
46	2-methyl-3-phenylpropanoic acid	99.30	206	0.41
47	1,1'-(1,2-ethenediyl)bis-benzene	100.32	180	1.07
48	1,1'-(2-butene-1,4-diyl)bisbenzene	102.10	208	1.31
49	2,5-diphenyl-1,5-hexadiene	103.42	234	0.84
50	1,6-diphenyl-1,5-hexadiene	114.69	234	0.60
51	tricyclo[9.2.2.2(4,7)heptadeca-1(14),2,4(17),5,7(16)-11(15),-12-heptaene ?	115.64	220	0.60

Pyrolysis of this polymer generates a considerable number of fragments similar to those of polystyrene. Styrene and styrene dimer are the main peaks in the pyrogram, accounting for 66.6% of the volatile compounds. Only a small amount of 2-methyl-2-propenoic acid is present, and a small amount of 2-methyl-3-phenylpropanoic acid (AB type compound) shows that the styrene and 2-methyl-2-propenoic acid are in some points connected. A few compounds detected in the pyrogram are nitriles. A small amount of 2,2'-azobis(2-methylpropanenitrile) or AIBN, probably used as radical initiator for the synthesis of the polymer, is seen in the pyrolysate. However, it is not clear if the other nitriles are the result of an excess of AIBN or of another impurity in the copolymer. Only one peak can be associated with heptaisobutyl-POSS group, and the corresponding spectrum is shown in Figure 6.7.45. Propenyl-heptaisobutyl-POSS, a likely fragment molecule, would have MW = 856, which is outside the range of masses used during the MS spectra acquisition in the Py-GC/MS study. Also, a proper assignment of different fragments in the mass spectrum is difficult to make. However, neutral losses of 14, 15, 28, 42 and 56 a.u. are numerous in the spectrum, which is consistent with the suggested structure.

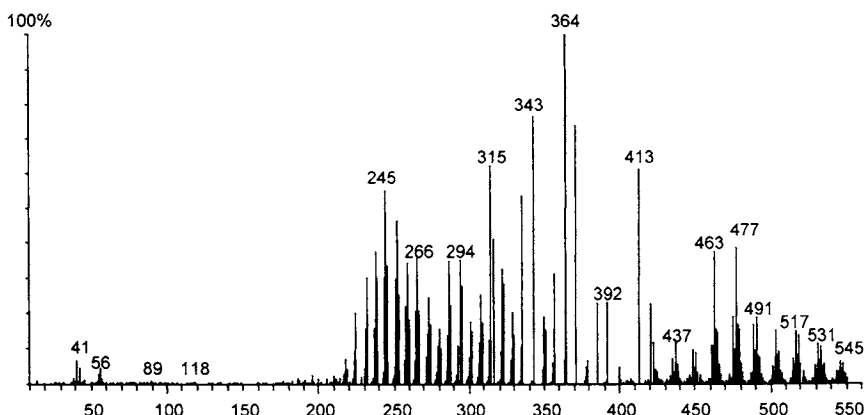


FIGURE 6.7.45. Mass spectrum of the peak eluting at 97.08 in the pyrogram from Figure 6.7.44. The spectrum is tentatively assigned to a compound related to propenyl-heptaisobutyl-POSS.

The GC/MS analysis of the pyrolysate composition does not provide any further proof of fragments of the octaalkylpentacyclo[9.5.1.1(3,9).1(5,15).1(7,13)]-octasiloxane group. It is very likely that this group is very stable at temperatures up to 600° C, and no smaller siloxane fragments are generated in the pyrolysate.

The pyrogram for poly(2-isopropenyl-2-oxazoline-co-methyl methacrylate) is shown in Figure 6.7.46 (see Table 4.2.2 for the experimental conditions), and the peak identification was done using MS spectral library searches only. The results are given in Table 6.7.31.

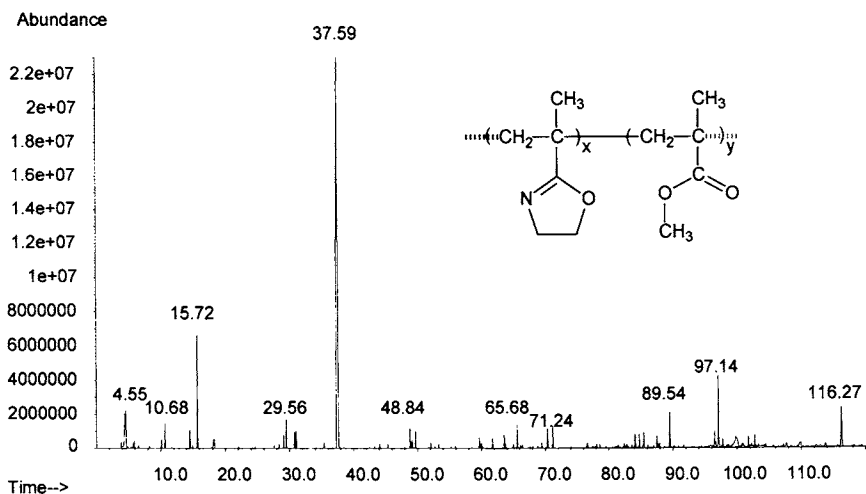


FIGURE 6.7.46. Result for a Py-GC/MS analysis of poly(2-isopropenyl-2-oxazoline-co-methyl methacrylate), $M_w = 40,000$. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 6.7.31. Compounds identified in the pyrogram of poly(2-isopropenyl-2-oxazoline-co-methyl methacrylate), $M_w = 40,000$, as shown in Figure 6.7.46.

Peak	Compound	Ret. Time	MW	Area %
1	carbon dioxide	4.40	44	trace
2	2-methylpropene	4.55	56	5.86
3	N-methyleneethanamine	5.71	57	trace
4	acetaldehyde	5.93	44	0.44
5	2,4-dimethyl-1,4-pentadiene	6.58	96	trace
6	isocyanatoethane	8.26	71	trace
7	2,5-dimethyl-1,5-hexadiene	10.18	110	0.49
8	methanol	10.68	32	1.38
9	2-methylpropanoic acid methyl ester	11.71	102	trace
10	2-methyl-2-propenenitrile	14.53	67	1.02
11	2-propenenitrile	14.93	53	trace
12	2-methyl-2-propenoic acid methyl ester (comonomer)	15.72	100	5.73
13	water	18.26	18	1.26
14	1,3-dimethylcyclopentane	24.23	98	trace
15	4,5-dihydro-2-methyloxazole	24.64	85	trace
16	dodecane (impurity)	27.64	170	trace
17	1-ethyl-2-methylpiperidine	28.38	127	trace
18	2-ethyl-4,5-dihydrooxazole	29.10	99	0.66
19	2,4-dimethyl-4-pentenoic acid methyl ester	29.32	142	trace
20	2,5-dimethyl-2-pyrrolidinone	29.56	113	1.48
21	1-dodecene (impurity)	30.84	168	0.84
22	5-vinyl-2H-1,3-oxazine ?	31.05	109	0.85
23	2-isopropenyloxazoline (comonomer)	37.59	111	54.34
24	2-(1-ethyl-1-methylprop-2-enyl)-1,3-oxazoline ?	48.84	153	1.04
25	C7H14-oxazoline derivative ?	49.17	167	0.45
26	2-(1-methylprop-2-enyl)-1,3-oxazoline	49.68	125	0.89
27	N,N'-dimethylbut-2-enamide	59.70	113	0.52
28	2-methylpropenoic acid	60.09	86	trace
29	unknown [41(100), 98(94), 150(86), 99(82), ..164(24)]	61.78		0.50
30	unknown [150(100), 151(65), 79(36), 136(35), 106(27)]	63.63		0.93
31	2-(1-methylvinyl)-1,3-oxazoline	65.68	111	1.20
32	methacrylamide	70.41	85	1.32
33	2-methyl-N,N-dimethylprop-2-enamide	71.24	113	1.26
34	mixture	84.14		0.91
35	unknown [165(100), 180(48), 137(41), 138(27), 151(25)]	84.79		0.85
36	unknown [165(100), 180(92), 124(75), 137(63), 138(45)]	85.49		1.15
37	unknown [167(100), 126(70), 85(58), 98(57), 181(41)]	87.52		0.87
38	unknown [166(100), 151(99), 69(62), 165(61), 137(47)]	89.54		2.55
39	unknown [69(100), 86(49), 41(45), 98(27), ...111(7)]	96.53		1.30
40	unknown [152(100), 181(97), 150(78), 221(44), 85(38)]	97.14		4.37
41	unknown [142(100), 69(45), 114(33), 56(27), 126(19)]	101.81		0.61
42	unknown [142(100), 69(54), 114(30), 56(30), 126(25)]	102.77		0.83
43	unknown [165(100), 67(19), 136(17), 137(17), 164(17)]	116.27		4.09

The pyrolysis of this copolymer takes place mainly as an unzipping process. The main pyrolysate components are 2-methyl-2-propenoic acid methyl ester and 2-isopropenyloxazoline. However, some other compounds are present in the pyrogram, with mass spectra that were not identified. Even the spectrum of 2-(1-methylprop-2-enyl)-1,3-oxazoline is not available in common mass spectral libraries and was only tentatively identified. The spectrum of this compound with some structures tentatively assigned for different ions is shown in Figure 6.7.47.

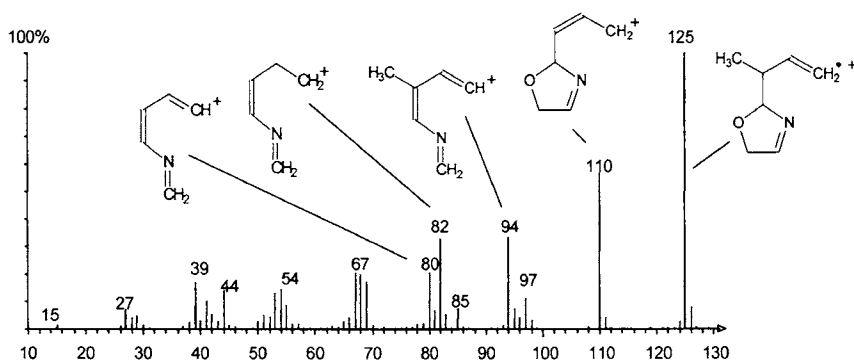


FIGURE 6.7.47. Mass spectrum tentatively assigned to 2-(1-methylprop-2-enyl)-1,3-oxazoline.

A few peaks in the pyrogram correspond to long chain hydrocarbons (dodecane, 1-dodecene). These were very likely impurities in the polymer.

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6.8 POLYMERS WITH SATURATED CARBON CHAIN AND KETONE GROUPS IN THE BACKBONE

- General aspects

The polymers from this class can be considered copolymers of carbon monoxide. The *alt*-copolymers that contain $-C(O)-$ groups can be viewed as homopolymers with a saturated carbon chain backbone. Among these are poly(ethylene-*alt*-carbon monoxide) CAS# 111190-67-1, poly(propene-*alt*-carbon monoxide-*alt*-ethylene) CAS# 121520-83-0, etc. More common are the copolymers with a variable ratio between hydrocarbon and CO, such as poly(ethylene-co-carbon monoxide) CAS# 25052-62-4, poly(ethylene-co-carbon monoxide-co-vinyl acetate), etc. In some cases, although an alternating polymer can be obtained, the mole ratio can be varied and both forms are available. For example, carbon monoxide and ethylene can form, using single stage autoclaving of ethylene and CO, a copolymer with the structure $(-CH_2CH_2-CO)_n-$ or a copolymer with the structure $[-(CH_2CH_2)_x-(CO)_y]_n-$. The same is true for poly(propene-co-carbon monoxide-co-ethylene), which can be obtained by free radical polymerization as an *alt*-copolymer or a polymer with the structure $[-(CH_2CH_2)_x-(CO)_y-(CH_2CH_2CH_2)_z]_n-$ [1].

Polymers from this class can be used for different practical purposes. For example, poly(ethylene-co-carbon monoxide) has better barrier properties for food packaging material than polyethylene, which is permeable for hydrophobic compounds used as flavors. Other copolymers can be used as plasticizers for nitrile rubber.

Thermal degradation of poly(ethylene-co-carbon monoxide) takes place by chain scission, yielding alkenes and ketone fragments. Around 500° C the decomposition products consist of CO, H₂O, ethene, and series of ketones with the general structure $R-[-CO-CH_2-CH_2-]_n-CO-R'$ where R, R' = -CH₃, -CH₂-CH₃ or -CH=CH₂ [2, 3].

- Olefins and styrene co carbon monoxide polymers

A number of copolymers of olefins and carbon monoxide were studied using analytical pyrolysis and reported in literature [4, 5]. In one study [4], the experiments were carried out at 550 °C with a THT of 10 s and with the separation of the pyrolysate on a methyl 5%-phenyl silicone (DB-5MS) column. The detection of peaks was done using a mass

spectrometer. The studied materials included several copolymers: ethylene-co-carbon monoxide obtained using ethylene and CO at three partial pressures (50/10, 30/30 and 10/50 atm.), poly(propylene-co-carbon monoxide), poly(propylene-*alt*-carbon monoxide), poly(styrene-co-carbon monoxide), and poly(*p*-*tert*-butylstyrene-co-carbon monoxide). These copolymers (except for poly(propylene-*alt*-carbon monoxide)) were obtained using the complex coordination catalysts $[\text{Pd}(\text{CH}_3\text{CN})_4]\text{BF}_4$. The peak identifications for the pyrolysis of poly(ethylene-co-carbon monoxide), 30/30 atm. ethylene/CO partial pressures, and for poly(ethylene-co-carbon monoxide), 50/10 atm. ethylene/CO partial pressures, are given in Table 6.8.1 [4].

TABLE 6.8.1. *Compounds identified in the pyrogram of poly(ethylene-co-carbon monoxide), 30/30 atm. ethylene/CO partial pressures, and poly(ethylene-co-carbon monoxide), 50/10 atm. ethylene/CO partial pressures, as reported in [4].*

No.	Compound	MW	30/30 atm.	50/10 atm.
1	CO-ethylene-H ₂ O	28, 28, 18	16.7	16.6
2	CH ₃ COCH ₃	58	1.3	1.3
3	CH ₂ =CHCOCH ₃	70	1.4	1.3
4	CH ₃ CH ₂ COCH ₃	72	2.8	2.8
5	CH ₃ CH ₂ COOCH ₃	88	0.3	0.2
6	CH ₂ =CHCOCH ₂ CH ₃	84	2.3	2.3
7	CH ₃ CH ₂ COCH ₂ CH ₃	86	2.3	2.3
8	dimethylfuran	96	0.8	0.9
9	ethylmethylfuran	110	1.4	1.5
10	C ₇ H ₈ O	108	0.8	0.9
11	cyclopentenone	82	0.7	0.7
12	C ₆ H ₈ O	96	0.3	0.3
13	C ₈ H ₁₂ O	124	0.8	0.8
14	2-methylcyclopentenone	96	0.5	0.5
15	C ₈ H ₁₀ O	122	0.9	1.0
16	CH ₃ COCH ₂ CH ₂ COCH ₃	114	0.6	0.6
17	C ₇ H ₈ O	108	0.5	0.5
18	3-methylcyclopentenone	96	1.7	1.7
19	C ₇ H ₁₀ O	110	0.2	0.2
20	phenol	94	0.2	0.2
21	CH ₃ COCH ₂ CH ₂ COOCH ₃	130	0.1	0.1
22	C ₇ H ₈ O	108	1.3	1.4
23	CH ₃ CH ₂ COCH ₂ CH ₂ COCH ₃	128	2.3	2.2
24	CH ₂ =CHCOCH ₂ CH ₂ COCH ₃	126	0.9	0.9
25	dimethylcyclopentenone	110	4.1	4.1
26	C ₇ H ₈ O	108	0.7	0.8
27	ethylcyclopentenone	110	1.4	1.4
28	cresol	108	0.9	1.0
29	CH ₃ CH ₂ COCH ₂ CH ₂ COOCH ₃	144	0.7	0.4
30	CH ₃ CH ₂ COCH ₂ CH ₂ COCH ₂ CH ₃	142	2.0	2.0
31	CH ₂ =CHCOCH ₂ CH ₂ COCH ₂ CH ₃	140	1.9	1.9
32	C ₈ H ₁₂ O	124	1.7	1.8
33	ethylphenol	122	1.5	1.6
34	C ₈ H ₁₀ O	122	0.9	0.9
35	C ₉ H ₁₂ O ₂	152	0.4	0.3
36	C ₈ H ₈ O ?	120	0.9	0.9
37	C ₁₀ H ₁₄ O ₂	166	0.2	0.2
38	C ₁₀ H ₁₄ O ₂	166	0.4	0.5
39	indanone	132	0.2	0.2

TABLE 6.8.1 (continued). Compounds identified in the pyrogram of poly(ethylene-co-carbon monoxide), 30/30 atm. ethylene/CO partial pressures, and poly(ethylene-co-carbon monoxide), 50/10 atm. ethylene/CO partial pressures, as reported in [4].

No.	Compound	MW	30/30 atm.	50/10 atm.
40	$C_{10}H_{12}O_2$	164	0.4	0.4
41	$C_9H_{12}O_2$	152	1.2	1.2
42	$C_{11}H_{16}O_2$	180	0.5	0.6
43	$C_{12}H_{14}O_2$	190	0.2	0.2
44	$CH_3(COCH_2CH_2)_2COCH_3$	170	0.7	0.6
45	$C_{11}H_{14}O_2$	178	0.3	0.3
46	$C_{10}H_{10}O$?	146	1.2	1.2
47	$C_{10}H_{14}O_2$	166	0.4	0.4
48	$C_{10}H_{12}O_2$	164	0.4	0.4
49	$C_{10}H_{14}O_2$	166	1.0	1.1
50	$C_{13}H_{14}O_2$	204	0.3	0.2
51	$C_{10}H_{10}O$?	146	1.1	1.2
52	$CH_3CH_2(COCH_2CH_2)_2COCH_3$	184	2.3	2.2
53	$CH_2=CH(COCH_2CH_2)_2COCH_3$	182	0.5	0.5
54	$C_{11}H_{14}O_2$?	160	0.50	0.6
55	$C_{11}H_{16}O_2$	180	0.60	0.6
56	$CH_3CH_2(COCH_2CH_2)_2COOCH_3$	200	1.0	0.8
57	$C_{11}H_{18}O$	178	0.5	0.5
58	$C_{14}H_{18}O$	218	0.2	0.2
59	$CH_3CH_2(COCH_2CH_2)_2COCH_2CH_3$	198	2.3	2.3
60	$CH_2=CH(COCH_2CH_2)_2COCH_2CH_3$	196	1.5	1.4
61	$C_{12}H_{16}O_3$	208	0.6	0.7
62	$C_{13}H_{12}O_2$	202	0.1	0.1
63	$C_{13}H_{14}O_2$	204	0.1	0.1
64	$C_{11}H_{14}O_2$	178	0.8	0.8
65	$C_{13}H_{18}O_3$	222	0.5	0.5
66	$C_{13}H_{18}O_3$	222	0.5	0.5
67	$C_{13}H_{16}O_3$	220	0.1	0.1
68	$C_{14}H_{20}O_3$	236	0.4	0.4
69	$C_{14}H_{18}O_3$	234	0.2	0.2
70	$CH_3(COCH_2CH_2)_3COCH_3$	226	0.6	0.6
71	$C_{14}H_{18}O_3$	234	0.7	0.7
72	$C_{13}H_{12}O_2$	202	0.4	0.4
73	$CH_3CH_2(COCH_2CH_2)_3COCH_3$	240	1.4	1.3
74	$CH_2=CH(COCH_2CH_2)_3COCH_3$	256	0.2	0.1
75	$C_{14}H_{16}O_2$	216	0.5	0.6
76	$CH_3CH_2(COCH_2CH_2)_3COCH_2CH_3$	254	1.5	1.5
77	$CH_2=CH(COCH_2CH_2)_3COCH_2CH_3$	252	1.0	1.0
78	$C_{16}H_{22}O_4$	278	0.8	0.7
79	$C_{17}H_{24}O_4$	292	0.9	0.9
80	$CH_3CH_2(COCH_2CH_2)_4COCH_3$	296	1.3	1.3
81	$CH_3CH_2(COCH_2CH_2)_4COCH_2CH_3$	310	1.5	1.4
82	$CH_3CH_2(COCH_2CH_2)_5COCH_3$	352	0.5	0.6
83	$CH_3CH_2(COCH_2CH_2)_5COCH_2CH_3$	366	0.6	0.7

A first observation regarding the results shown in Table 6.8.1 is that there are only minor differences in the pyrolysis products of the 30/30 and the 50/10 copolymers. The products consist of several small molecules (H_2O , CO , C_2H_4), ketones, ketoesters, and cyclic compounds. Their proportions are given in Table 6.8.2 [4].

TABLE 6.8.2. Classification of compounds shown in Table 6.8.1 generated from the pyrolysis of poly(ethylene-co-carbon monoxide), 30/30 atm. ethylene/CO partial pressures, and from poly(ethylene-co-carbon monoxide), 50/10 atm. ethylene/CO partial pressures.

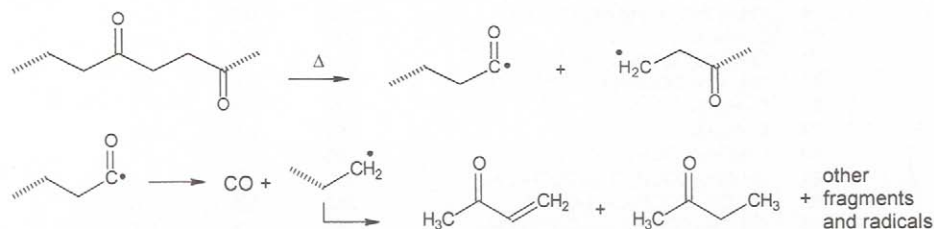
Class of compounds	Compound	30/30 atm.	50/10 atm.
light products	H ₂ O, CO, C ₂ H ₄	16.7	16.6
monoketones	CH ₃ COCH ₃ , CH ₂ =CHCOCH ₃ , CH ₃ CH ₂ COCH ₃ , CH ₂ =CHCOCH ₂ CH ₃ , CH ₃ CH ₂ COCH ₂ CH ₃	10.1	10.0
diketones	MW = 114, 126, 128, 140, 142	7.7	7.6
triketones	MW = 170, 182, 184, 196, 198	7.3	7.0
tetraketones	MW = 226, 240, 252, 254	4.5	4.4
pentaketones	MW = 296, 310	2.8	2.7
hexaketones	MW = 352, 366	1.1	1.3
ketoesters	MW = 88, 130, 144, 200	2.4	1.6
cyclic compounds		38.8	40.1

The same types of compounds were generated in the pyrolysis of poly(propylene-*alt*-carbon monoxide). The pyrolysis products also consist of several small molecules (H₂O, CO, C₃H₆), ketones, and cyclic compounds. Their proportions are given in Table 6.8.3 [4].

TABLE 6.8.3. Classification of compounds for the pyrolysis of poly(propylene-*alt*-carbon monoxide).

Class of compounds	Compound	wt%
light products	CO, C ₃ H ₆ , H ₂ O	35.4
monoketones	MW = 58, 70, 72, 84, 86, 98, 100, 112, 114	12.8
diketones	MW = 128, 140, 142, 154, 156, 168, 170, 182, 184	7.0
cyclic compounds		35.9

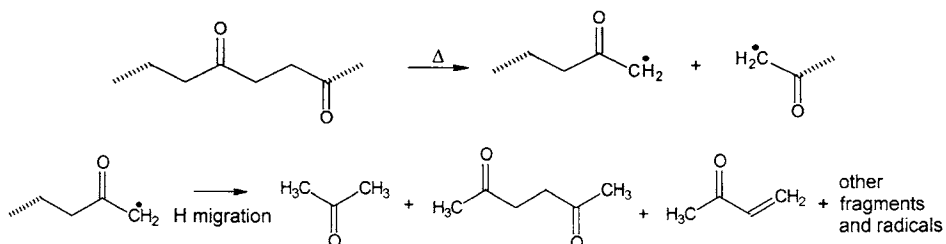
The pyrolysate components of both copolymers show similar mechanisms of the reaction. Both C(O)—CH₂ and CH₂—CH₂ bonds can be cleaved. For example, in the case of poly(ethylene-co-carbon monoxide), the reactions taking place with C(O)—CH₂ cleavage are shown schematically below:



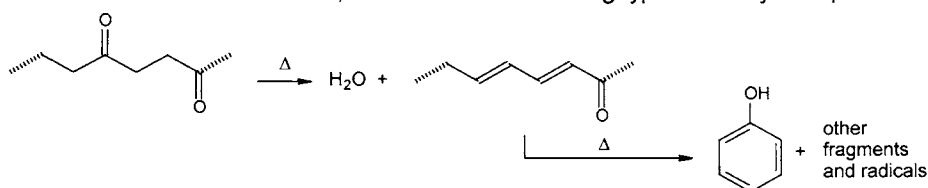
Cyclization reactions also can occur, for example through bite back type reactions as shown below for the formation of cyclopentenone:



The cleavage of $\text{CH}_2\text{--CH}_2$ can be described schematically by the following reactions:



Some aromatic compounds also are formed, also through hydrogen migration and by the elimination of some water molecules. The presence of these compounds indicates that under the influence of heat, reactions of the following type also may take place:



The resulting aromatic rings also can have attached CH_3 , or C_2H_5 groups, depending on where the cleavage of the carbon chain takes place.

In a different study [5], alternating copolymers of carbon monoxide, ethylene, styrenes, and norbornadienes and their modified polymers with primary amines, P_2S_5 and P_2O_5 were prepared, pyrolyzed at 550 °C for 10 s, and analyzed by GC/MS. Py-GC/MS confirmed that the ketonic groups in the alternating copolymers were converted by treatment with primary amines, P_2S_5 , or P_2O_5 into pyrrole-, thiophene-, or furan-containing chains, respectively. The oxygen-containing groups, which remained intact during the modification with P_2S_5 , were detected in small amounts in the pyrolysates. Pyrolysis GC/MS for analytical purposes after derivatization of the CO copolymers also was reported [6].

Similar to the poly(olefin-*alt*-carbon monoxide), polymers alternating styrene or a substituted styrene unit and CO also are reported in literature [7]. The idealized structure of these types of polymers is shown below:

- Terpolymers of olefins, styrene, and carbon monoxide

Several terpolymers of ethylene, propylene, and CO, and also of ethylene, styrene and CO were studied using Py-GC/MS [4].

The composition of the pyrolysate of two ethylene, propylene, CO terpolymers are given in Table 6.8.4. Terpolymer A was reported to be obtained from ethylene at 10 atm., propylene 1.5 g, and CO at 30 atm. Terpolymer B was reported to be obtained from ethylene at 20 atm., propylene 1.5 g, and CO at 30 atm. [4]. The synthesis of the terpolymers is detailed in literature [8, 9].

TABLE 6.8.4. *Classification of compounds from the pyrolysis of ethylene (E) propylene (P) and CO terpolymer*

Compound type	Origin*	Terpoly. A wt %	Terpoly. B wt %
linear monoketones	P-CO	8.0	2.8
linear monoketones	E-CO, P-CO	9.1	10.8
linear di- and triketones	E-CO	9.1	13.0
cyclic compounds	E-CO	12.5	30.5
cyclic compounds	P-CO	12.0	8.7

* P-CO indicates propylene-CO sequence, and E-CO indicates ethylene-CO sequence.

The composition of the pyrolysate of two ethylene, styrene, CO terpolymers are given in Table 6.8.5. Terpolymer C was reported to be obtained from ethylene at 15 atm., styrene 1.1 g, and CO at 30 atm. Terpolymer D was reported to be obtained from ethylene at 5 atm., styrene 1.0 g, and CO at 30 atm. [4].

TABLE 6.8.5. *Classification of compounds from the pyrolysis of ethylene (E) styrene (S) and CO terpolymer*

Compound type	Examples	Origin*	Terpoly. C wt %	Terpoly. D wt %
small molecules	H ₂ O, CO, C ₂ H ₄	E-CO, S-CO	8.5	5.4
monoketones (aliphatic)	MW = 58, 70, 72, 84, 86	E-CO	3.6	1.2
diketones (aliphatic)	MW = 114, 126, 128, 140, 142	E-CO	1.9	0.2
triketones (aliphatic)	MW = 198	E-CO	0.4	0.2
ketoesters (aliphatic)	MW = 88, 144	E-CO	0.3	0.2
alicyclic compounds		E-CO	8.6	1.8
aromatic hydrocarbons	styrene, ethylbenzene, toluene, methylstyrenes, etc.	E-CO, S-CO	33.0	44.1
aromatic ketones		S-CO	9.6	14.9
aromatic esters	PhCH=CHCOOCH ₃ , PhCH ₂ CH ₂ COOCH ₃	S-CO	0.5	0.8
cyclic compounds from junction points	MW = 158, 172, 184, 186, 198, 200, 248, 262	E-CO/S-CO	14.7	10.2

* E-CO indicates ethylene-CO sequence and S-CO indicates styrene-CO sequence.

The results shown in Tables 6.8.4 and 6.8.5 show that the type of compounds generated by pyrolysis of the terpolymers are similar to those obtained from the simple copolymers. Fragment polyketones of different lengths resulting from the fragmentation of the backbone are the typical pyrolysis products. The aliphatic or aromatic groups associated with the C=O groups appear in the pyrolysate depending on the sequence of monomeric units present in the macromolecule. Similar to the pyrolysate of simple copolymers, the presence of water and of aromatic hydrocarbons indicates that some side chain eliminations also occur.

References 6.8

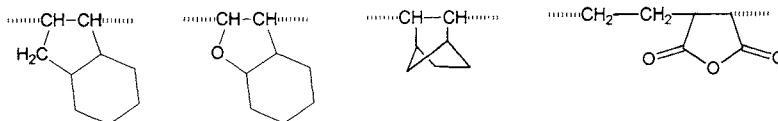
1. A. Sommazzi, F. Garbassi, *Prog. Polym. Sci.*, 22 (1997) 1547.
2. J. C. W. Chien, A. X. Zhao, *Polym. Degrad. Stab.*, 40 (1993) 257.
3. O. Chiantore, M. Lazzari, F. Ciardelli, S. De Vito, *Macromolecules*, 30 (1997) 2589.
4. F. Bertini, G. Audisio, J. Kiji, A. Yamada, M. Hatano, Y. Yuasa, *J. Anal. Appl. Pyrol.*, 64 (2002) 279.
5. J. Kiji, T. Okano, T. Chiyoda, F. Bertini, G. Audisio, *J. Anal. Appl. Pyrol.*, 40–41 (1997) 331.
6. F.C.-Y. Wang, D. L. Hasha, *Anal. Chem.*, 71 (1999) 1131.
7. Y. Feng, J. Sun, Y. Zhu, W. Chen, *J. Polym. Sci., A: Polym. Chem.*, 35 (1997) 1283.
8. F. Bertini, G. Audisio, J. Kiji, *J. Anal. Appl. Pyrol.*, 49 (1999) 31.
9. J. Kiji, A. Yamada, F. Bertini, G. Audisio, *Macromol. Rapid Commun.*, 22 (2001) 598.

6.9 OTHER POLYMERS WITH SATURATED CARBON CHAIN BACKBONE

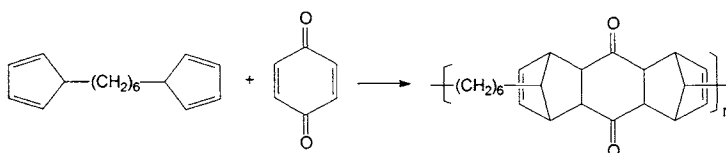
- General aspects

Several less common polymers with saturated carbon chain backbone are commercially available and have special practical applications. For example, indene obtained from the coal-tar oil by-products of coking operations can be polymerized by the addition of H_2SO_4 to form a linear hydrocarbon type polymer with relatively low DP [1–3]. The polymerization of coumarone from the same source generates a similar product, which is used in coatings, adhesives, etc.

Polymers with saturated carbon chain backbone can be obtained from the polymerization of a variety of unsaturated compounds such as norbornylene, which generates poly(1,3-cyclopentylenevinylene), etc. Other polymers with a saturated carbon backbone can be obtained as copolymers between maleic anhydride and an alkene. Although these types of compounds are technically copolymers, their uniform structure makes them similar to homopolymers such as in the example of poly(ethylene-*alt*-maleic anhydride). Formulas of some polymers with saturated carbon chain backbone from this class are shown below:



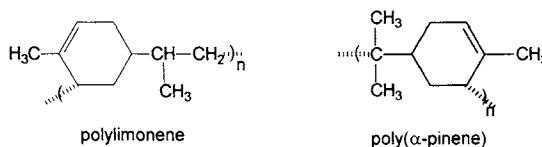
In addition to the polymers that have a linear carbon backbone, which are still related to polyethylene having various substituents on the carbon chain, other polymers possessing only carbon atoms in the backbone are known, but they have a more complicated structure. For example, the Diels-Alder condensation of a bisdiene and benzoquinone takes place as follows:



The resulting polymer has a carbon chain backbone, but it is different from common vinyl or vinylidene polymers.

- Polyterpenes

A rather different type of macromolecule is generated from the polymerization of certain terpenes such as limonene and α -pinene. The polymers generated from these compounds retain a double bond in the structure of the molecule, and it can be argued that they have a mixed saturated and unsaturated carbon chain backbone as shown below:



The presence of the double bonds in the polymer allows crosslinking. This process is applied in practice to prepolymers with groups allowing additional binding, which leads to thermosetting polymers. The results for a Py-GC/MS analysis of polylimonene (or polydipentene), CAS# 70750-53-7, are shown in Figure 6.9.1. The pyrolysis was done at 600° C in He at a heating rate of 10° C/ms. The separation was done on a Carbowax column (60 m, 0.32 mm i.d., 0.32 μ m film thickness) with the GC starting at 40° C with a ramp of 2° C/min. up to 240° C and a final oven time of 20 min. (see Table 4.2.2). The MS was operated in EI+ mode. The peak identification for the chromatogram shown in Figure 6.9.1 was done using MS spectral library searches only and is given in Table 6.9.1.

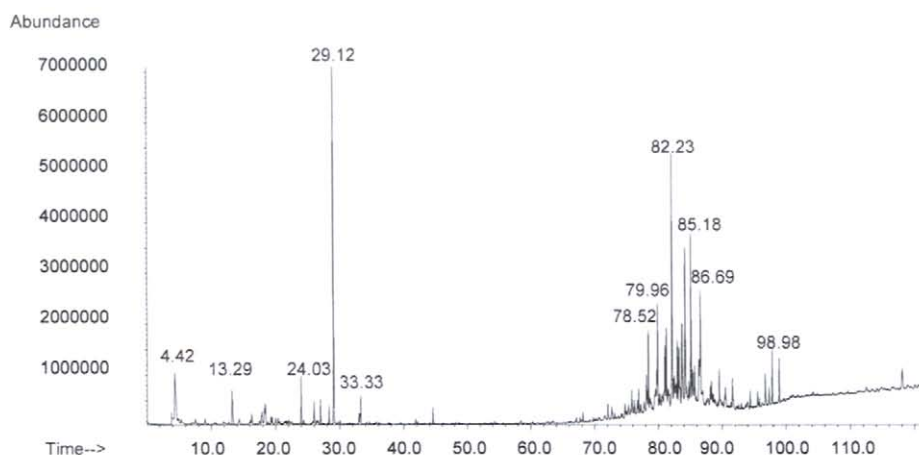


FIGURE 6.9.1. Result for a Py-GC/MS analysis of polylimonene (or polydipentene). Pyrolysis done from 0.4 mg sample, at 600° C in He, with the separation on a Carbowax type column.

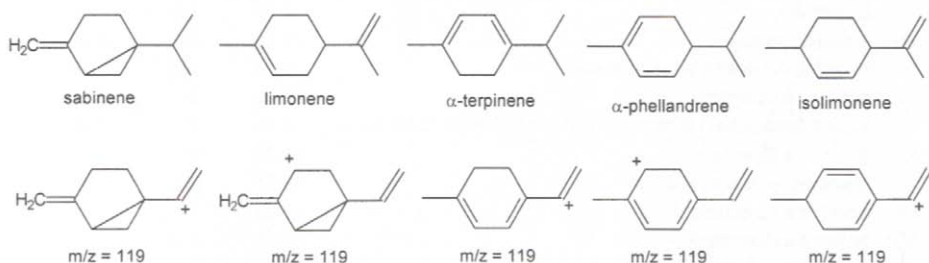
TABLE 6.9.1. Compounds identified in the pyrogram of polylimonene as shown in Figure 6.9.1.

Peak	Compound	Ret. Time	MW	Area %
1	propane	4.33	44	1.38
2	1-propene	4.42	42	2.77
3	2-methyl-1-butene	4.64	70	1.38
4	4-methyl-1,3-pentadiene	7.54	82	trace
5	2-methyl-cyclohexene	9.06	96	trace
6	1-methyl-1,4-cyclohexadiene	13.29	94	1.47
7	1-methyl-4-(1-methylethyl)-cyclohexane	16.32	140	trace
8	m-menth-1(6)-ene or 1-methyl-5-(1-methylethyl)cyclohexene	18.43	138	trace
9	3-methyl-5-(1-methylethyl)cyclohexene	20.00	138	trace
10	1-methyl-4-(1-methylethyl)cyclohexene	24.03	138	1.52
11	α -phellandrene or 2-methyl-5(methylethyl)cyclohexa-1,3-diene	26.04	136	0.85
12	α -terpinene or 1-methyl-4-(1-methylethyl)-1,3-cyclohexadiene	27.04	136	0.85
13	limonene or 1-methyl-4-(1-methylethyl)cyclohexene	28.34	136	0.57
14	sabinene or 4-methylene-1-(1-methylethyl)bicyclo[3.1.0]hexane	29.12	136	11.30
15	isolimone or 4-methyl-1-(1-methylethyl)cyclohexene	33.02	136	trace
16	1-methyl-4(1-methylethyl)benzene	33.33	134	1.55
17	1-methyl-4-(1-methylethyl)benzene	44.60	132	trace
18	unknown hydrocarbon	75.88	228 ?	1.39
19	unknown hydrocarbon	76.96	272 ?	0.83
20	unknown hydrocarbon	78.20	274 ?	1.69
21	dimer of a dipentene	78.52	272	3.96
22	dimer of a dipentene	79.96	272	6.79
23	dimer of a dipentene	81.10	272	4.27
24	dimer of a dipentene	81.34	274	3.00
25	dimer of a dipentene	82.23	272	9.60
26	dimer of a dipentene	82.57	272	1.98
27	dimer of a dipentene	83.04	272	2.31

TABLE 6.9.1 (continued). *Compounds identified in the pyrogram of polylimonene as shown in Figure 6.9.1.*

Peak	Compound	Ret. Time	MW	Area %
28	dimer of a dipentene	83.31	274	3.14
29	dimer of a dipentene	83.78	274	3.77
30	dimer of a dipentene	84.27	272	7.49
31	dimer of a dipentene	85.18	272	6.07
32	unknown hydrocarbon	85.42		2.11
33	dimer of a dipentene	85.77	272	1.45
34	dimer of a dipentene	86.69	272	6.28
35	dimer of a dipentene	88.39	272	1.61
36	unknown hydrocarbon	89.61		1.71
37	dimer of a dipentene	91.68	270	1.84
38	dimer of a dipentene	96.80	270	1.57
39	dimer of a dipentene	97.88	270	1.89
40	dimer of a dipentene	98.98	270	1.59

The pyrolysate of polylimonene, as seen from the pyrogram shown in Figure 6.9.1, consists of some small fragment molecules (such as propane, propene, etc.) and mono and diterpenes as well as their dimers. It is very likely that larger fragments also are generated, but they do not elute from the chromatographic column in the conditions the experiment was performed. Terpenes (dipentenes) are rather sensitive to heating, and this may explain the variety of monoterpenes detected in the pyrolysate. In an even larger number in the pyrolysate are the dimers of dipentenes (diterpenes). The most common fragment ion in the mass spectrum of various dipentene dimers indicated in Table 6.9.1 is $m/z = 119$. This ion may be generated from fragments of the dimers with structures related to the monoterpenes seen earlier in the pyrogram, such as sabinene, α -phellandrene, α -terpinene, limonene, isolimonene, etc. The structures of some monoterpenes and some possible ions with $m/z = 119$ generated from the diterpenes are shown below:



A similar polymer to polylimonene is poly(α -pinene), CAS# 70750-57-1. The polymer contains one double bond per monomeric unit, which may allow further crosslinking. Poly(α -pinene) also can be part of various copolymers or polymer blends, for example, with polypropylene [4]. The pyrolysis of a poly(α -pinene) sample performed in the same conditions as for polylimonene generates the pyrogram shown in Figure 6.9.2. The peak identification for the chromatogram shown in Figure 6.9.2 was done using MS spectral library searches only and is given in Table 6.9.2.

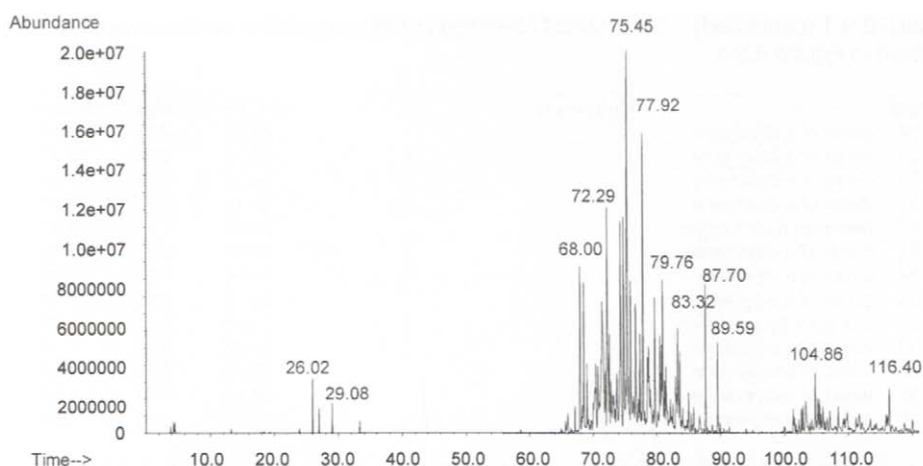


FIGURE 6.9.2. Result for a Py-GC/MS analysis of poly(α -pinene). Pyrolysis done from 0.4 mg sample, at 600° C in He, with the separation on a Carbowax type column.

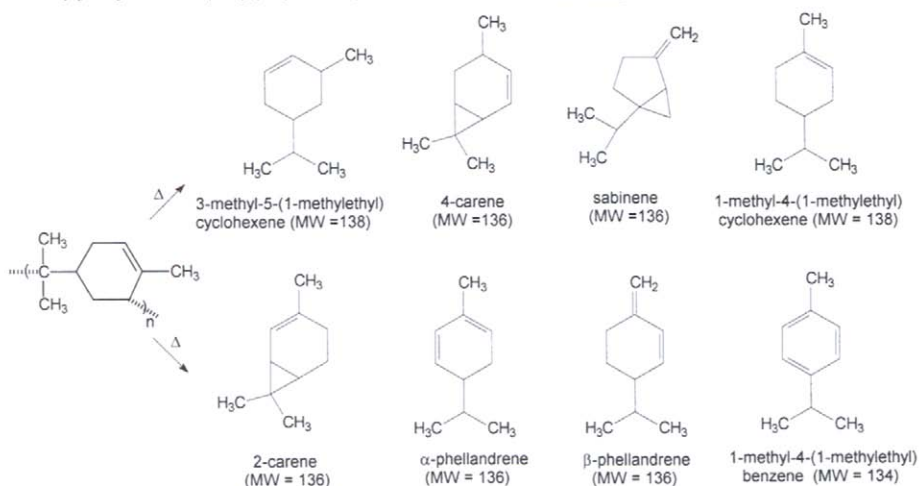
TABLE 6.9.2. Compounds identified in the pyrogram of poly(α -pinene) as shown in Figure 6.9.2.

Peak	Compound	Ret. Time	MW	Area %
1	5,5-dimethyl-1,3-cyclopentadiene	13.32	94	trace
2	3-methyl-5-(1-methylethyl)cyclohexene	19.92	138	trace
3	4-carene	21.50	136	trace
4	sabinene	23.85	136	trace
5	1-methyl-4-(1-methylethyl)cyclohexene	23.97	138	trace
6	α -phellandrene	26.03	136	1.01
7	2-carene	27.03	136	0.43
8	β -phellandrene	29.08	136	0.53
9	1-methyl-4(1-methylethyl)benzene	33.34	134	0.43
10	dimer of a dipentene	67.16	272	0.54
11	1,2,3,4-tetrahydro-1,6-dimethyl-4-(1-methylethyl)naphthalene	68.01	202	4.52
12	dimer of a dipentene	68.39	272	0.60
13	unknown, similar to peak 11	68.61	202	3.41
14	dimer of a dipentene	69.08	272	1.29
15	dimer of a dipentene	72.30	272	7.54
16	dimer of a dipentene	74.38	272	9.29
17	similar to a dimer of a diterpene (one less double bond)	74.89	274	6.95
18	dimer of a dipentene	75.48	272	13.45
19	dimer of a dipentene	75.98	272	3.85
20	similar to a dimer of a diterpene (one less double bond)	76.75	274	4.80
21	dimer of a dipentene	77.41	272	2.63
22	dimer of a dipentene	77.94	272	9.14
23	dimer of a dipentene	78.79	272	3.23

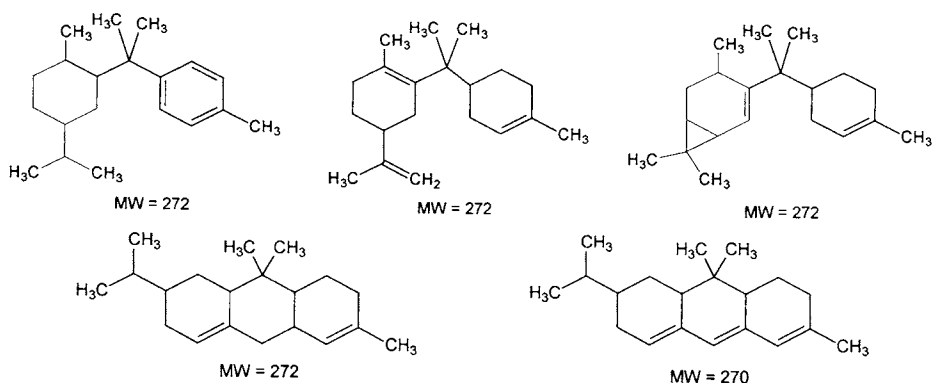
TABLE 6.9.2 (continued). Compounds identified in the pyrogram of poly(α -pinene) as shown in Figure 6.9.2.

Peak	Compound	Ret. Time	MW	Area %
24	dimer of a dipentene	79.76	272	3.74
25	dimer of a dipentene	80.55	272	2.87
26	dimer of a dipentene	80.81	272	2.09
27	dimer of a dipentene	81.02	272	3.67
28	dimer of a dipentene	83.32	272	3.04
29	similar to a dimer of a diterpene (one additional double bond)	87.71	270	3.23
30	trimer of a diterpene	104.86	410	1.84
31	similar to a trimer (one additional double bond)	105.51	408	1.47
32	similar to a trimer (one additional double bond)	107.12	408	0.74
33	similar to a trimer (one additional double bond)	108.45	408	0.69
34	similar to a trimer (one additional double bond)	116.41	408	1.70
35	trimer of a diterpene	119.96	410	1.30

Many peaks in the pyrogram of poly(α -pinene) were not positively identified. The pyrogram showed three groups of peaks, one group consisting of a few dipentenes, the second consisting of dimers of dipentenes that dominate the chromatogram, and the third of a few trimers of dipentenes. The formation of some of the dipentenes identified in the pyrolysate of poly(α -pinene) is shown in the following scheme:



Several hypothetical structures of the dimers of dipentenes ($C_{20}H_{32}$ or $C_{20}H_{30}$) that may explain the mass spectra common in the pyrogram of poly(α -pinene) are shown below:



The current mass spectral libraries (NIST 2002, Wiley 7) do not contain the spectra of these compounds, and therefore they were not identifiable by the MS library searches. The use of mass spectrum fragments can be of help in these situations. One example is the tentative identification for the peak with retention time of 75.48 min. (from Figure 6.9.2) as 4-methyl-1-{1-methyl-1-[2-methyl-5-(methylethyl)cyclohexyl]ethyl}benzene. The fragment assignments for the ions seen in the mass spectrum are shown in Figure 6.9.3.

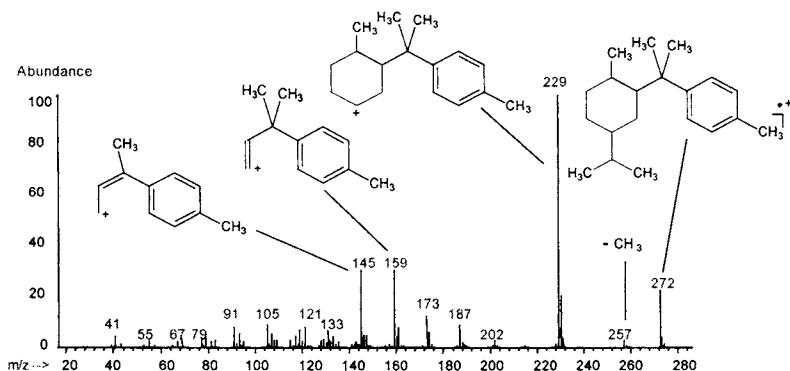
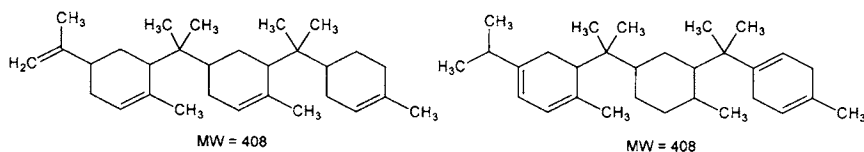


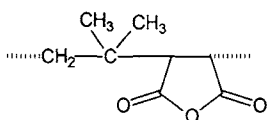
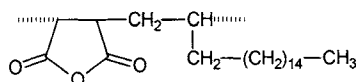
FIGURE 6.9.3. Mass spectrum and possible assignments for the fragments for the peak eluting at 75.48 min. in the pyrogram shown in Figure 6.9.2.

Hypothetical structures also can be given for the trimers of dipentenenes. Two examples, from many other possible structures that can explain the mass spectra, are shown below for the compounds with MW = 408 in the pyrogram of poly(α -pinene):



- Poly(alkenes-*alt*-maleic anhydride)

Several copolymers of maleic anhydride, such as poly(ethylene-*graft*-maleic anhydride), and poly(propylene-*graft*-maleic anhydride) were discussed in Section 6.1. Another subgroup of copolymers having maleic anhydride as comonomer is that of *alt*-copolymers with alkenes. Since *alt*-copolymers are similar to homopolymers of an AB type monomer, these macromolecules are discussed separately. The polymers from this group have hydrophilic properties in contrast with polyalkenes, which are highly hydrophobic. For this reason, poly(alkenes-*alt*-maleic anhydride) polymers can be water soluble or form gels in water, being used as viscosity modifiers for solutions, suspensions and emulsions. Since these polymers are not toxic and are biodegradable, they have numerous applications in cosmetics, adhesives, etc. Various alkenes can form *alt*-copolymers with maleic anhydride, including ethylene, isobutylene, and even alkenes with a long aliphatic chain such as octadecene or with attached aromatic rings such as stilbene. The idealized formulas of poly(isobutylene-*alt*-maleic anhydride) and of poly(maleic anhydride-*alt*-1-octadecene) are shown below:

Poly(isobutylene-*alt*-maleic anhydride)Poly(maleic anhydride-*alt*-1-octadecene)

Some information regarding thermal stability of this type of polymer is available in literature. These polymers typically generate CO₂, some maleic anhydride, and fragments related to the olefin. For example, poly(maleic anhydride-*co-trans*-stilbene) (alternating), when heated from ambient to 500° C, generates CO₂, styrene, maleic anhydride; small amounts of benzene, cyclohexadiene, dimethylbutene, ethylcyclobutanol, and 4-methoxystyrene. Major decomposition products for this polymer are chain fragments (79%), including aromatic, ketonic and unsaturated structures [5].

The results for a Py-GC/MS analysis of a sample of poly(ethylene-*alt*-maleic anhydride) CAS# 9006-26-2, with M_w = 100,000–500,000 are shown in Figure 6.9.4. The pyrolysis was done at 600° C in He at a heating rate of 10° C/ms, TAT = 10 s, and the separation was done on a Carbowax column in identical conditions as for other examples previously discussed (see Table 4.2.2). The MS was operated in EI+ mode. The peak identification for the chromatogram shown in Figure 6.9.4 was done using MS spectral library searches only and is given in Table 6.9.3.

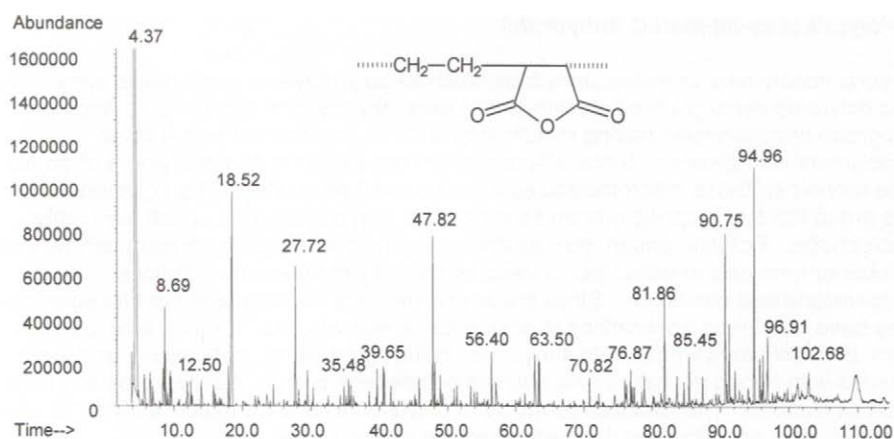


FIGURE 6.9.4. Result for a Py-GC/MS analysis of poly(ethylene-alt-maleic anhydride) $M_w = 100,000$ –500,000. Pyrolysis done from 0.4 mg sample, at 600° C in He, with the separation on a Carbowax type column.

TABLE 6.9.3. Compounds identified in the pyrogram of poly(ethylene-alt-maleic anhydride) $M_w = 100,000$ –500,000 as shown in Figure 6.9.4.

Peak	Compound	Ret. Time	MW	Area %
1	carbon dioxide	4.37	44	57.54
2	cyclopentene	5.71	68	0.72
3	1,3-cyclopentadiene	6.58	66	0.66
4	1,3,5-hexatriene	8.48	80	0.77
5	2-methyleneheptane	8.69	112	1.60
6	3-methyl-3-heptene	8.78	112	0.82
7	2-methyl-2-heptene	9.49	112	0.54
8	1,3-cyclohexadiene	9.63	80	0.55
9	5,5-dimethyl-1,3-cyclopentadiene	12.00	94	0.56
10	trans, trans-1,3,5-heptatriene	12.50	94	0.36
11	1,3-cycloheptadiene	14.03	94	0.51
12	bicyclo[4.1.0]hept-2-ene	15.78	94	trace
13	toluene	18.00	92	0.65
14	water	18.52	18	6.70
15	1,4-dimethylbenzene	24.52	106	trace
16	cyclopentanone	27.72	84	2.10
17	2-methylcyclopentanone	28.22	98	trace
18	1-ethyl-3-methylbenzene	30.32	120	trace
19	styrene	32.48	104	trace
20	1,2,4-trimethylbenzene	34.20	120	trace
21	2-ethyl-cyclopentanone	34.80	112	trace
22	5-methyl-2-cyclopenten-1-one	35.48	96	0.40
23	2,4-dimethyl-2-cyclopenten-1-one	38.45	110	trace
24	2-cyclopentenone	39.65	82	0.56

TABLE 6.9.3 (continued). Compounds identified in the pyrogram of poly(ethylene-*alt*-maleic anhydride) $M_w = 100,000$ – $500,000$ as shown in Figure 6.9.4.

Peak	Compound	Ret. Time	MW	Area %
25	2-methyl-2-cyclopenten-1-one	40.55	96	0.62
26	indane	40.65	118	0.94
27	2-propylcyclopentanone	41.65	126	trace
28	acetic acid	45.35	60	trace
29	2,3-dimethyl-2-cyclopenten-1-one	45.82	110	0.40
30	2-ethyl-1-hexanol	47.82	130	2.28
31	indene	48.11	116	0.68
32	butanoic acid	56.41	88	0.84
33	2-propenoic acid	57.07	72	0.60
34	2,4-dimethyl-2,5-furandione	62.80	126	1.37
35	3-ethyl-4-methyl-2,5-furandione	63.37	140	0.91
36	2,4-diethyl-2,5-furandione	63.50	154	0.79
37	2,3-dimethyl-4-hydroxy-2-butenolactone	70.82	112	0.44
38	3-methyl-2(3H)-benzofuranone	76.03	148	0.41
39	2,3,4,5,6,7-hexahydro-1H-inden-1-one	76.30	136	trace
40	2-methylphenol	76.87	108	0.55
41	4,4a,5,6-tetrahydro-7-methyl-2(3H)-naphthalenone	78.86	162	0.67
42	3-methylene-2-oxo-cyclohexanecarboxylic acid methyl ester ?	81.86	168	1.92
43	unknown [150(100), 79(73), 55(61), 107(54), 121(26), 122(23)]	85.45		0.77
44	unknown [150(100), 79(44), 59(37), 41(27), 107(24)]	87.44		0.52
45	unknown [150(100), 79(57), 121(24), 94(22), 122(13), 107(13)]	90.75		3.08
46	3-tertbutyl-2-cyclohexen-1-one ?	91.33	152	1.45
47	2,3,5,6-tetramethyl- <i>p</i> -benzoquinone ?	94.96	164	4.26
48	unknown [163(100), 178(80), 149(69), 79(30), 91(21)]	96.91		1.47

As seen from the pyrogram and the peak identification given in Figure 3.8.4 and Table 3.8.3, respectively, the pyrolysis of poly(ethylene-*alt*-maleic anhydride) gives different compounds compared to polyethylene. Only some small molecules are hydrocarbons, and only a small amount of 2,4-dimethyl-2,5-furandione was detected in the pyrogram. Maleic anhydride itself was not detected. The major peak in the pyrogram is that of carbon dioxide. One oxygen atom remaining per monomer unit after CO₂ elimination forms several oxygenated compounds including alcohols and phenols.

A rather similar pyrogram is obtained and a similar path is followed during the pyrolysis of poly(isobutylene-*alt*-maleic anhydride), CAS# 26426-80-2. A sample of this polymer with $M_w = 60,000$ was pyrolyzed at 600° C in He in similar conditions as for poly(ethylene-*alt*-maleic anhydride). The pyrogram is shown in Figure 6.9.5, and the peak identification obtained by MS spectral library searches only is given in Table 6.9.4.

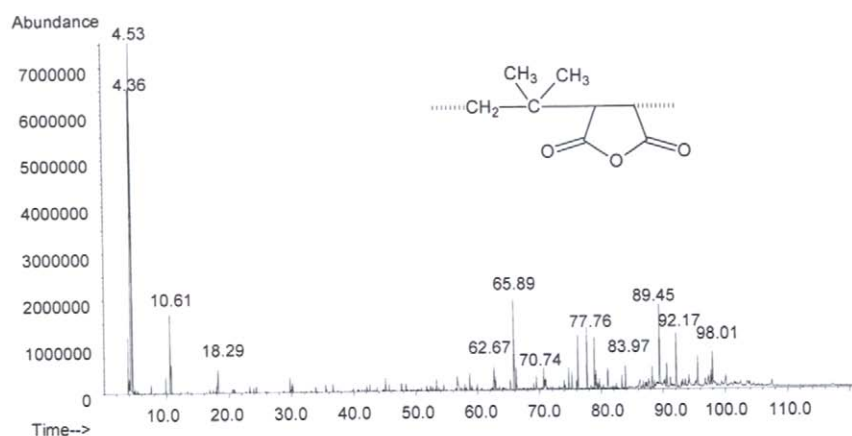


FIGURE 6.9.5. Result for a Py-GC/MS analysis of poly(isobutylene-alt-maleic anhydride) $M_w = 60,000$. Pyrolysis done from 0.4 mg sample, at 600° C in He, with the separation on a Carbowax type column.

TABLE 6.9.4. Compounds identified in the pyrogram of poly(isobutylene-alt-maleic anhydride) $M_w = 60,000$ as shown in Figure 6.9.5.

Peak	Compound	Ret. Time	MW	Area %
1	methylcyclopropane	4.08	56	trace
2	carbon dioxide	4.36	44	28.81
3	2-methyl-1-propene	4.53	56	22.13
4	2-methyl-1,3-pentadiene	7.55	82	trace
5	acetic acid ethyl ester	9.92	88	trace
6	2-methyl-2-propanol	10.61	74	6.40
7	5,5-dimethyl-2-ethyl-1,3-cyclopentadiene	13.04	122	trace
8	1,3-cyclopentadiene	14.03	94	trace
9	toluene	18.00	92	trace
10	water	18.52	18	1.91
11	3-methylene-1,5,5-trimethylcyclohexane	20.87	136	trace
12	ethylbenzene	23.32	106	trace
13	1,3-dimethylbenzene	24.40	106	trace
14	1,4-dimethylbenzene	24.52	106	trace
15	2-ethenyl-1,3,3-trimethylcyclohexene	28.78	150	trace
16	1,2,5,5-tetramethyl-1,3-cyclopentadiene	29.78	122	trace
17	4-(1-methylethyl)benzaldehyde ?	30.06	148	trace
18	1-ethyl-4-(1-methylethyl)benzene	33.91	148	trace
19	3,5,5-trimethylcyclohexene ?	35.50	124	trace
20	2,3,4-trimethyl-2-cyclopenten-1-one	36.67	124	trace
21	3,4,5,5-tetramethyl-2-cyclopenten-1-one	42.14	138	trace
22	acetic acid	45.35	60	trace
23	2-methyl-5-(1-methylethyl)phenol	48.40	150	trace
24	5-isopropenyl-2-methylcyclopent-1-enecarboxaldehyde	52.67	150	trace
25	2-propenoic acid	57.07	72	trace
26	3-methylbutenoic acid	58.71	102	trace
27	3,3-dimethylbutanoic acid	59.93	116	trace
28	3-methyl-4-propyl-2,5-furandione	62.67	154	1.58

TABLE 6.9.4 (continued). Compounds identified in the pyrogram of poly(isobutylene-*alt*-maleic anhydride) $M_w = 60,000$ as shown in Figure 6.9.5.

Peak	Compound	Ret. Time	MW	Area %
29	3,3-dimethyl-2-(3-methyl-1,3-butandienyl)cyclopentanone	65.26	178	trace
30	3-methyl-2-butenic acid	65.89	100	6.38
31	4-methylpentanoic acid	66.28	116	1.48
32	5-methyl-2,4-diisopropylphenol	69.54	192	trace
33	2,4-bis(1-methylethyl)phenol	70.74	178	1.28
34	2,3,3,4,7-pentamethyl-2,3-dihydro-benzofuran	74.79	190	1.10
35	unknown [164(100), 93(78), 81(67), 121(46), 149(29)]	76.28		3.34
36	4-hydroxy-2-methylacetophenone ?	77.76	150	3.86
37	5-(1,1-dimethylethyl)-1,3-benzodioxol-2-one	78.96	192	2.87
38	unknown [178(100), 192(92), 149(85), 80(66), 121(64), 219(61)]	83.97		1.43
39	unknown [191(100), 206(79), 163(68), 55(34), 91(30), 107924]	88.26		1.35
40	3-(tert-butyl)-3-hydrobenzo[b]furan-2-one	89.45	190	5.79
41	unknown [205(100), 220(61), 161(42), 191(25), 105(17), 176(17)]	90.61		1.91
42	8-isopropylidene-bicyclo[4.3.0]nonan-2-one	92.17	178	3.79
43	4,8a-dimethyl-6-(methylethyl)-1,2,3,7,8,8a-hexahydronaphthalene	95.59	204	2.30
44	next homolog of 4,8a-dimethyl-6-(methylethyl)-1,2,3,7,8,8a-hexahydronaphthalene	98.01	218	2.27

The list of compounds from Table 6.9.4 shows good similarity to that from Table 6.9.3, a number of compounds being homologs (within one or two CH_2 groups).

Pyrolysis of another poly(alkene-*alt*-maleic anhydride), where the alkene has a very long alkyl chain, gives a different pyrogram although the thermal cleavage of the macromolecule may take place similarly. This is shown in Figure 6.9.6, which gives the pyrogram of poly(maleic anhydride-*alt*-1-octadecene), CAS# 25266-02-8. Pyrolysis and pyrolysate analysis were done for this polymer in the same conditions as for the other poly(alkenes-*alt*-maleic anhydride) previously discussed (see Table 4.2.2). Table 6.9.5 shows some of the peak identifications, based on MS searches, for Figure 6.9.6.

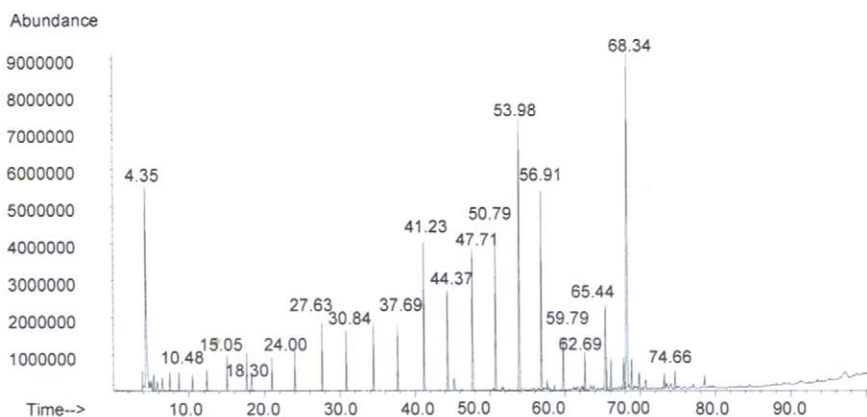


FIGURE 6.9.6. Result for a Py-GC/MS analysis of poly(maleic anhydride-*alt*-1-octadecene) $M_n = 30,000$ – $50,000$. Pyrolysis done from 0.4 mg sample, at 600°C in He, with the separation on a Carbowax type column.

TABLE 6.9.5. Compounds identified in the pyrogram of poly(maleic anhydride-*alt*-1-octadecene) $M_n = 30,000$ –50,000 as shown in Figure 6.9.6.

Peak	Compound	Ret. Time	MW	Area %
1	carbon dioxide	4.35	44	11.54
2	ethylcyclopropane ?	4.81	70	trace
3	hexane	5.06	86	trace
4	1-hexene	5.37	84	0.77
5	heptane	5.86	100	trace
6	1-heptene	6.50	98	trace
7	octane	7.51	114	0.78
8	1-octene	8.68	112	0.80
9	nonane	10.48	128	0.61
10	1-nonene	12.38	128	0.79
11	decane	15.05	142	1.18
12	1-decene	17.64	140	1.21
13	water	18.30	18	0.79
14	undecane	20.98	156	1.01
15	1-undecene	24.01	154	1.20
16	dodecane	27.63	170	1.99
17	1-dodecene	30.84	168	1.73
18	tridecane	34.47	184	1.99
19	1-tridecene	37.69	182	1.91
20	tetradecane	41.23	198	4.99
21	1-tetradecene	44.37	196	3.06
22	acetic acid	45.35	60	trace
23	pentadecane	47.71	212	5.07
24	1-pentadecene	50.79	210	4.92
25	hexadecane	53.98	226	13.10
26	1-hexadecene	56.91	224	7.45
27	2-propenoic acid	57.07	72	trace
28	heptadecane	59.79	240	1.99
29	1-heptadecene	62.69	238	1.31
30	octadecane	65.44	254	4.49
31	?-octadecene	65.55	252	0.82
32	?-octadecene	66.14	252	1.25
33	?-octadecene	67.83	252	1.41
34	1-octadecene	68.34	252	18.49
35	5-octadecene	68.91	252	1.21
36	?-octadecene	69.90	252	0.68
37	nonadecane	70.74	268	trace
38	?-nonadecene	73.25	266	0.72
39	?-octadecadiene	74.66	250	0.72
40	?-eicosene	78.57	280	trace

Besides carbon dioxide, 2-propenoic acid, and acetic acid, all the other compounds seen in the pyrogram are alkanes and alkenes resulting from the side chain of the hydrocarbon monomer unit. A detailed inspection of the traces in the pyrogram shows very low levels of some of the same compounds formed during pyrolysis of poly(ethylene-*alt*-maleic anhydride) or poly(butylene-*alt*-maleic anhydride), although they are not listed in Table 6.9.5. For example, some alkyl benzenes are present in the pyrolysate of poly(maleic anhydride-*alt*-1-octadecene), but at about five times lower levels than in poly(butylene-*alt*-maleic anhydride) pyrolysate, where alkyl benzenes were listed as trace. The mass ratio of maleic anhydride/butene is 1.75, while that of maleic anhydride/1-octadecene is about 0.39, which explains the lower presence of the

compounds generated from the maleic anhydride moiety in the pyrolysate of poly(maleic anhydride-*alt*-1-octadecene).

- Other polymers with saturated carbon chain backbone

An example of a pyrogram of poly(indene-co-coumarone), 10 % coumarone, CAS# 35343-70-5 with $M_w = 420,000$, is shown in Figure 6.9.7. The pyrolysis was done at 600° C in He with separation of a Carbowax column and MS detection, similarly to other polymers previously discussed in this book (see also Table 4.2.2). The identification of the peaks was done using MS library search only, and it is indicated in Table 6.9.6.

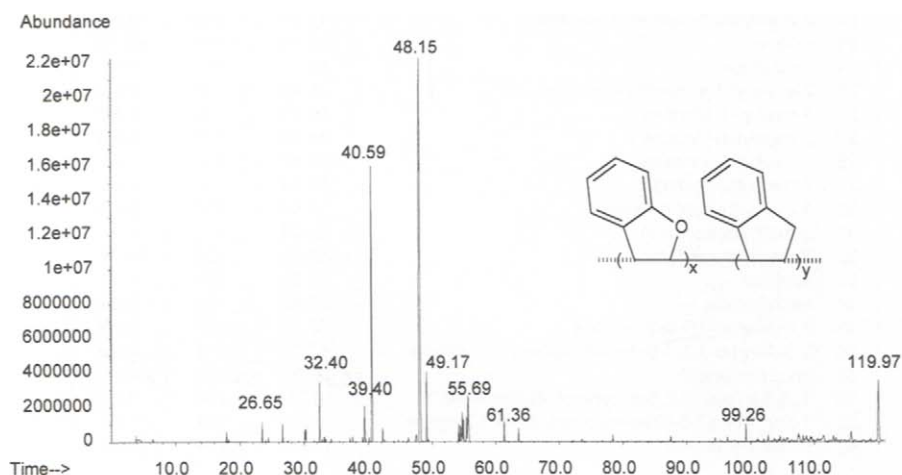


FIGURE 6.9.7. Pyrogram from a Py-GC/MS analysis of poly(indene-co-coumarone) 10% coumarone $M_w = 420,000$. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

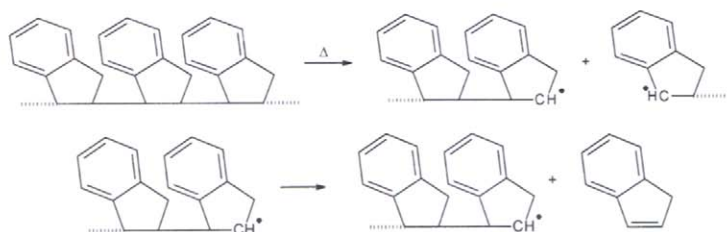
TABLE 6.9.6. Compounds identified in the pyrogram of poly(indene-co-coumarone) $M_w = 420,000$ shown in Figure 6.9.7.

Peak	Compound	Ret. Time	MW	Area%
1	cyclopentene	5.64	68	trace
2	1,3-cyclopentadiene	6.49	66	trace
3	toluene	17.92	92	0.54
4	ethylbenzene	23.48	106	0.98
5	1,4-dimethylbenzene	24.43	106	trace
6	(1-methylethyl)benzene	26.65	120	0.84
7	1-methyl-2-ethylbenzene	30.08	120	trace
8	1-methyl-3-ethylbenzene	30.25	120	1.20
9	styrene	32.40	104	2.89
10	1-methyl-2-(1-methylethyl)benzene	33.14	134	trace
11	1-methyl-3-(1-methylethyl)benzene	33.34	134	trace
12	1,2,3-trimethylbenzene	34.18	120	trace

TABLE 6.9.6 (continued). Compounds identified in the pyrogram of poly(indene-co-coumarone) $M_w = 420,000$ shown in Figure 6.9.7.

Peak	Compound	Ret. Time	MW	Area%
13	1-ethyl-3,5-dimethylbenzene	37.14	134	trace
14	α -methylstyrene (1-methylethenyl)benzene	37.59	118	trace
15	1-ethenyl-3-methylbenzene	39.40	118	2.37
16	1-ethenyl-2-methylbenzene	40.59	118	18.52
17	1-ethenyl-4-ethylbenzene	42.27	132	0.64
18	2-propenylbenzene	42.54	118	trace
19	methyl(1-methylethenyl)benzene	44.01	132	trace
20	1-methyl-2-(2-propenyl)benzene	44.68	132	trace
21	2-ethenyl-1,3-dimethylbenzene	46.29	132	trace
22	2,3-dihydro-5-methyl-1H-indene	47.51	132	0.54
23	indene	48.15	116	46.89
24	benzofuran	49.17	118	3.55
25	2-ethenyl-1,4-dimethylbenzene	49.44	132	trace
26	1-methyl-1H-indene	54.21	130	0.85
27	3-methyl-1H-indene	54.48	130	trace
28	2-methyl-1H-indene	54.51	130	1.41
29	7-methylbenzofuran	54.74	132	2.52
30	1,2-dihydronaphthalene	54.93	130	trace
31	3-methylbenzofuran	55.44	132	trace
32	2-methylbenzofuran	55.69	132	4.74
33	azulene	61.36	128	1.11
34	naphthalene	63.62	128	0.68
35	2,3-dihydro-1H-inden-1-one	78.39	132	trace
36	2,3-dihydro-1,1,3-trimethyl-3-phenyl-1H-indene	87.51	236	trace
37	benzylindane ?	99.26	208	0.91
38	1,3,5-trimethyl-2,6-di(cyclopentyl)benzene ?	107.45	256	1.31
39	1-phenyl-4-(3,5-dimethylphenyl)buta-1,3-diene ?	115.69	234	1.03
40	indan-2-ylindane	119.97	234	6.49

The results of the analysis of the volatile part of the pyrolysate show that the copolymer generates about 47% indene and about 3.5% of benzofuran. Another major component in the pyrolysate is 1-ethenyl-2-methylbenzene. It is likely that the pyrolysis is initiated by random scission and leads to the formation of the monomer as indicated in the reactions shown below



The formation of benzofuran takes place similarly. Other fragment molecules are the result of some hydrogen transfer reactions, such as in the case of 1-ethenyl-2-methylbenzene. The dimer related compound indan-2-ylindane is also detected in the pyrolysate, although its identification is only tentative since the spectrum of this

compound is not available in common mass spectral libraries. The spectrum tentatively assigned to this compound is shown in Figure 6.9.8. The ion fragments tentatively assigned for the peaks in the mass spectrum also are shown in the figure.

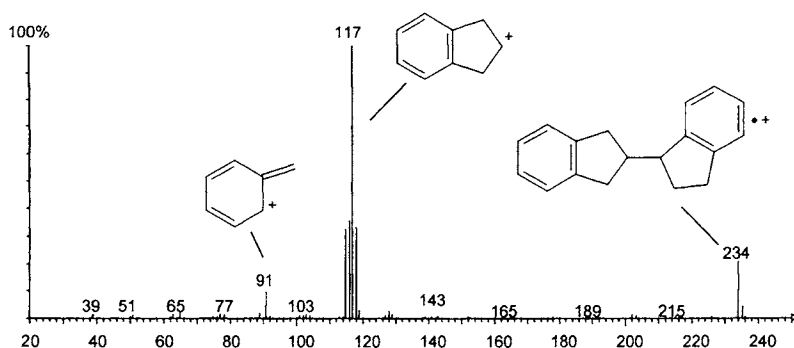


FIGURE 6.9.8. Mass spectrum tentatively identified as generated by indan-2-ylindane (MW = 234).

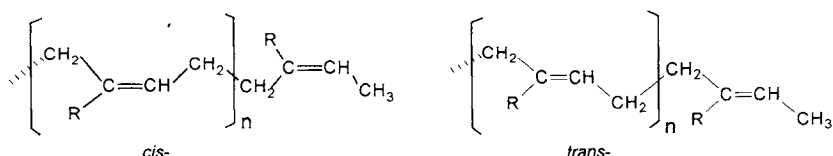
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CHAPTER 7

*Polymers with Unsaturated Carbon Chain Backbone***7.1 UNSATURATED POLYHYDROCARBONS****- General aspects**

A number of molecules with two conjugated double bonds, such as 1,3-butadiene or 2-methyl-1,3-butadiene (isoprene), can undergo a 1-4 polymerization with the migration of the double bond in the 2 position. The resulting polymer contains isolated double bonds, but their presence leads to the possibility of having *cis*- and *trans*- forms, as shown below:



Polyisoprene ($\text{R} = \text{CH}_3$) with a *cis*-1,4 configuration is common in nature in different species of plants and is known as natural rubber. *Trans*-polyisoprene is found in two natural resins known as gutta-percha and balata. Natural or synthetic polyisoprenes, as well as polybutadiene, are among the most common elastomers with many practical uses. Other elastomers with extensive practical applications are copolymers, many of them using butadiene or isoprene in the starting monomer mixture.

An important property of the polymers containing carbon-carbon double bonds in the backbone is their capability to be vulcanized. *Vulcanization* is, in general terms, the process of introduction of some crosslinking bridges between the polymer molecules. It has as a main physical effect a considerable extension of the temperature range where the polymer has good elasticity. The temperatures at which vulcanized elastomer begins to decompose are higher. Other positive effects are achievable by vulcanization, such as an increase in the tensile strength. Vulcanization is typically done by adding 0.5–5% sulfur to the polymer, followed by heating at 130–145° C and mixing, usually in the presence of an accelerator. Nonsulfur vulcanization processes also are known. Some aspects regarding pyrolysis of vulcanized unsaturated polyhydrocarbon type homopolymers are discussed in Section 7.2.

A different subclass of unsaturated hydrocarbon type polymers is formed by polyacetylenes. This type of polymer contains conjugated double bonds in a linear structure, and due to their special electrical properties they have been the subjects of numerous studies including some on thermal stability.

Various other polymers have double bonds in their carbon backbone. Some are polyhydrocarbons such as poly- α -pinene (see Section 6.8), while others are polymers including aromatic cycles in the backbone or possibly heteroatoms. These polymers are typically classified under different groups (see Chapters 8 and 15).

- Poly(butadiene) and poly(isoprene)

1,4-Polybutadiene, CAS# 9003-17-2, is a common synthetic polymer with the formula $(-\text{CH}_2\text{CH}=\text{CHCH}_2-)_{\text{n}}$. The *cis* form (CAS# 40022-03-5) of the polymer can be obtained by coordination or anionic polymerization. It is used mainly in tires blended with natural rubber and synthetic copolymers. The *trans* form is less common. 1,4-Polyisoprene in *cis* form, CAS# 9003-31-0, is commonly found in large quantities as natural rubber, but also can be obtained synthetically, for example, using the coordination or anionic polymerization of 2-methyl-1,3-butadiene. Stereoregular synthetic *cis*-polyisoprene has properties practically identical to natural rubber, but this material is not highly competitive in price with natural rubber, and its industrial production is lower than that of other unsaturated polyhydrocarbons. Synthetic *trans*-polyisoprene, CAS# 104389-31-3, also is known. Pyrolysis and the thermal decomposition of these polymers has been studied frequently [1–18]. Some reports on thermal decomposition products of polybutadiene and polyisoprene reported in literature are summarized in Table 7.1.1 [19].

TABLE 7.1.1. Summary regarding literature studies on thermal decomposition of polybutadiene and polyisoprene.

Polymer	Temp. °C	Results	Ref.
poly(butadiene)	325–475	14.1% of products are volatile at 25° C including 1.5% of monomer among other saturated and unsaturated hydrocarbons; 85.9% of products are larger fragments nonvolatile at 25° C	20–23
poly(butadiene)	20° C/min. 15% weight loss	effect of <i>cis/trans</i> ratio; increasing <i>trans</i> content gives more cyclopentene and 1,3-cyclohexadiene and less 4-vinyl-1-cyclohexene and 1,3-butadiene	24
poly(isoprene) 97% <i>cis</i> -1,4; 3% 3,4	384	in helium; methane (0.04 wt.%), ethylene (0.08), ethane (0.03), propylene (0.15), propane (0.06), isobutylene (0.09), 1- and 2-butenes (0.07), methyl butene (0.09), isoprene (29), toluene (0.02), 2,3-dimethyl cyclopentene (1.2), octene (0.05), 2,4-dimethyl cyclohexene (0.16), <i>m</i> -xylene (0.33), 1-methyl-4-ethyl cyclohexene (0.18), 1,5-dimethyl-5-vinyl cyclohexene (2.5), dipentene (60), C ₁₁ H ₁₈ (0.2), C ₁₂ H ₁₈ (0.2), C ₁₅ H ₂₄ (3.5), C ₁₆ H ₂₆ (1.8)	25
poly(isoprene) synthetic	287–400	3.4% Isoprene, 8.8% dipentene, small amounts of <i>p</i> -menthene.	26–28

The results for a Py-GC/MS analysis of polybutadiene (*cis*), $(-\text{CH}_2\text{CH}=\text{CHCH}_2-)_{\text{n}}$, CAS# 40022-03-5, with $M_w = 2,000,000\text{--}3,000,000$ are shown in Figure 7.1.1. The pyrolysis was done at 600° C in He at a heating rate of 20° C/ms with 10 s THT similar to other examples previously discussed. Also, the separation was done on a Carbowax column (see Table 4.2.2) in a GC/MS system with the mass spectrometer operating in EI+ mode. The peak identification for the chromatogram shown in Figure 7.1.1 was done using MS spectral library searches only and is given in Table 7.1.2.

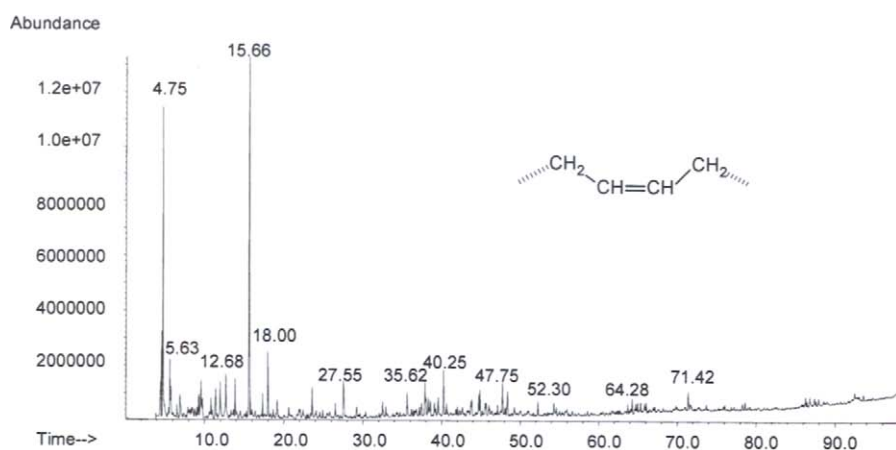


FIGURE 7.1.1. Pyrogram from a Py-GC/MS analysis of a polybutadiene (cis) sample with $M_w = 2,000,000$ – $3,000,000$. Pyrolysis done on 0.4 mg material at 600°C in He, with the separation on a Carbowax type column.

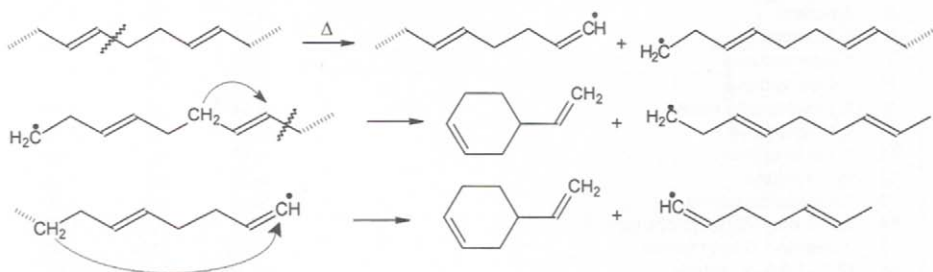
TABLE 7.1.2. Compounds identified in the pyrogram of polybutadiene (cis) with $M_w = 2,000,000$ – $3,000,000$ shown in Figure 7.1.1.

Peak	Compound	Ret. Time	MW	Area %
1	ethane	4.37	30	trace
2	1-propene	4.43	42	1.56
3	2-methylpropene	4.55	56	2.49
4	1-butene	4.59	56	2.29
5	2-butene	4.62	56	2.23
6	1,3-butadiene	4.75	54	13.12
7	1,3-pentadiene	5.69	68	2.80
8	1,4-pentadiene	5.88	68	1.39
9	1,3-cyclopentadiene	6.54	66	0.79
10	1,4-hexadiene	6.89	82	2.15
11	1,3,5-hexatriene	8.46	80	trace
12	cyclohexene	9.27	82	1.22
13	1,3-cyclohexadiene	9.62	80	3.20
14	E,Z-3-ethylidenecyclohexene ?	9.75	108	1.02
15	3-methyl-1,6-heptadiene	10.82	110	1.05
16	(?,?)-1,3,6-octatriene	11.35	108	0.91
17	3-methyl-1,5-heptadiene	11.42	110	1.50
18	2,6-octadiene	11.95	110	2.89
19	benzene	12.68	78	3.53
20	ethenylcyclohexane	13.85	110	1.85
21	4-ethenylcyclohex-1-ene	15.66	108	22.61
22	(Z,E)-1,3,5-octatriene	17.33	108	1.08
23	toluene	18.00	92	3.88
24	2,3-dimethyl-1,3-cyclohexadiene	19.18	108	1.06

TABLE 7.1.2 (continued). Compounds identified in the pyrogram of polybutadiene (*cis*) with $M_w = 2,000,000 - 3,000,000$ shown in Figure 7.1.1.

Peak	Compound	Ret. Time	MW	Area %
25	ethylbenzene	23.57	106	1.96
26	1,3-dimethylbenzene	24.60	106	trace
27	(<i>trans</i>)-2,4,6-octatriene	26.53	108	0.95
28	1,4-dimethylbenzene	27.55	106	2.48
29	propylbenzene	29.31	120	0.61
30	styrene	32.61	104	0.97
31	1-methyl-4-ethylbenzene	33.11	120	trace
32	4-methylene-tricyclo[5,2,1,0E2,6]decane	35.62	148	1.93
33	1,5-diethenyl-3-methyl-2-methylenecyclohexane	37.88	162	2.05
34	1,4-divinyl-octahydopentalene	38.32	162	1.01
35	1-cyclohexylpentadiene	39.57	150	1.22
36	spiro[2.9]dodeca-4,8-diene ?	40.25	162	2.69
37	indane	40.65	118	0.66
38	spiro[2.9]dodeca-5,9-diene ?	43.86	162	0.82
39	2,6-diethenyl- <i>cis</i> -cyclooctene ?	44.91	162	1.48
40	2,6-diethenyl- <i>cis</i> -cyclooctene isomer	47.75	162	2.30
41	spiro[2.9]dodeca-4,8-diene isomer	48.40	162	1.67
42	(<i>E,E,E</i>)-1,4,8-dodecatriene	52.30	162	0.83
43	3-methyl-1H-indene	54.31	130	0.72
44	naphthalene	63.87	128	trace
45	unknown cycloalkene	71.42		1.06

The pyrolysis of butadiene generates a relatively low level of monomer (13–14%) as indicated in Table 7.1.1. A larger proportion of small molecules is formed by 4-ethenyl-1-cyclohexene, which is generated from bite back type reactions, as shown below (hydrogen migration is indicated by arrows):



Pyrolysis results for a polybutadiene sample phenyl terminated (45% wt. vinyl) with $M_n = 1,000$ and about 10% *trans*-1,4 and 5% *cis*-1,4 is shown in Figure 7.1.2. The pyrolysis was done in similar conditions with the other polybutadiene sample. The peak identification for the pyrogram is given in Table 7.1.3

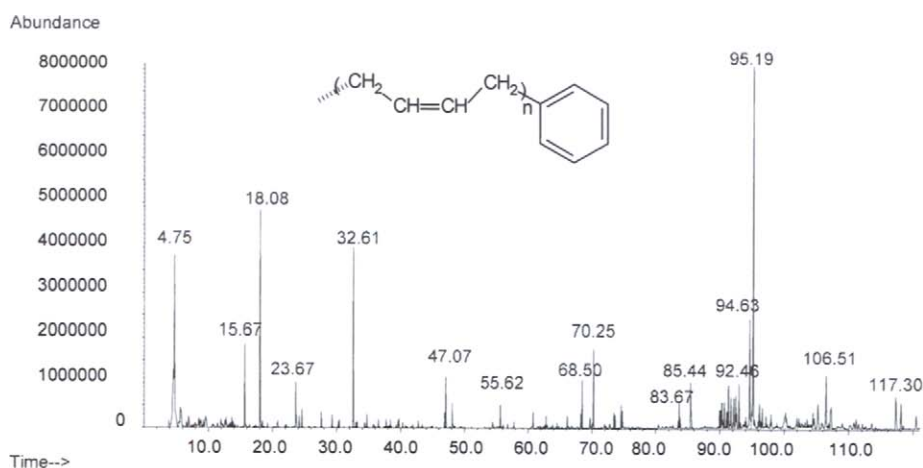


FIGURE 7.1.2. Pyrogram from a Py-GC/MS analysis of a polybutadiene sample phenyl terminated (45% wt. vinyl) with $M_n = 1,000$ and about 10% trans-1,4 and 5% cis-1,4. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 7.1.3. Compounds identified in the pyrogram of a polybutadiene sample phenyl terminated (45% wt. vinyl) with $M_n = 1,000$ and about 10% trans-1,4 and 5% cis-1,4 and shown in Figure 7.1.2.

Peak	Compound	Ret Time	MW	Area%
1	methane	4.33	16	0.11
2	ethene	4.50	28	0.32
3	1-propene	4.54	42	1.86
4	2-butene	4.62	56	2.29
5	1,3-butadiene	4.75	54	4.42
6	1-pentene	4.82	70	1.22
7	2-pentene	4.92	70	0.58
8	1,3-pentadiene	5.69	68	1.35
9	1,4-pentadiene	5.88	68	1.35
10	1-methyl-1,3-cyclopentadiene	8.54	80	1.00
11	1,3-cyclohexadiene	9.62	80	1.27
12	2,6-octadiene	11.95	110	1.22
13	benzene	12.68	80	1.11
14	5,5-dimethyl-1,3-cyclopentadiene	13.66	94	0.11
15	ethenylcyclohexane	13.85	110	0.11
16	4-ethenylcyclohex-1-ene	15.67	108	3.14
17	1,5-dimethyl-1,4-cyclohexadiene	16.60	108	0.88
18	toluene	18.08	92	7.11
19	2,5,5-trimethylcyclopentadiene	20.69	108	0.11
20	ethylbenzene	23.67	106	1.82
21	1,2-dimethylbenzene	24.20	106	1.07
22	1,3-dimethylbenzene	24.60	106	1.07
23	1,4-dimethylbenzene	27.55	106	0.88

TABLE 7.1.3 (continued). Compounds identified in the pyrogram of a polybutadiene sample phenyl terminated (45% wt. vinyl) with $M_n = 1,000$ and about 10% *trans*-1,4 and 5% *cis*-1,4 and shown in Figure 7.1.2.

Peak	Compound	Ret Time	MW	Area%
24	propylbenzene	29.31	120	0.86
25	1-methyl-2-ethylbenzene	30.30	120	0.11
26	1-methyl-3-ethylbenzene	30.66	120	0.11
27	styrene	32.61	104	5.06
28	1-methyl-4-ethylbenzene	33.11	120	0.11
29	2-propenylbenzene	33.41	118	0.11
30	1,5-diethyl-3-methyl-2-methylene-cyclohexane	34.76	162	0.86
31	1,2,3,4,4a,8a-hexahydronaphthalene	36.60	134	0.11
32	α -methylstyrene	37.73	118	0.11
33	1-ethenyl-3-methylbenzene	39.73	118	1.04
34	3-butenylbenzene	39.93	132	0.11
35	1-ethyl-3,5-dimethylbenzene	40.38	134	0.11
36	indane	40.72	118	trace
37	3-pentenylbenzene	42.74	146	0.11
38	pentylbenzene	43.22	148	0.11
39	C6-benzene	45.66	162	0.53
40	4-pentenylbenzene	46.91	146	0.95
41	5-phenyl-2-pentene	47.07	146	2.29
42	3-methyl-2-butenylbenzene	48.10	146	0.95
43	1-phenyl-2,4-pentadiene	54.55	144	0.11
44	2,3-dimethyl-1H-indene	55.62	144	0.98
45	hexa-3,5-dienylbenzene	57.75	158	0.56
46	hexa-2,5-dienylbenzene	60.78	158	0.99
47	C5-indene	62.82	186	0.99
48	naphthalene	63.87	128	trace
49	C5-indene	66.18	186	0.99
50	benzene-C9-diene	68.29	200	1.51
51	benzene-C9-diene	68.50	200	1.04
52	hydrocarbon type	69.74		1.04
53	benzene-C9-diene	70.25	200	2.61
54	benzene-C9-diene	74.59	200	0.86
55	benzene-C10-triene	83.67	212	1.71
56	benzene-C10-triene	85.44	212	2.19
57	benzene-C11-triene	90.32	226	2.56
58	benzene-C12-triene	91.35	240	1.46
59	benzene-C12-triene	91.74	240	1.46
60	benzene-C13-triene	92.46	254	1.96
61	benzene-C13-triene	94.63	254	4.60
62	benzene-C13-triene	95.19	254	13.41
63	benzene-C14-tetraene	106.51	266	4.47
64	benzene-C14-tetraene	109.03	266	2.58
65	benzene-C15-tetraene	111.54	280	1.53
66	benzene-C16-tetraene	117.30	294	2.39

The pyrogram for the phenyl-terminated polymer is rather different from that of pure polybutadiene shown in Figure 7.1.1. This is the result of a high content of phenyl end groups. Except for the fragment resulting from the end fragments of the polymer, other molecular fragments are identical (e.g., butadiene, 1,3-pentadiene, 4-ethenyl-cyclohex-1-ene, etc.).

Another homopolymer analyzed by Py-GC/MS and discussed below is polyisoprene (*cis*), with the formula $[-CH_2CH=C(CH_3)CH_2-]_n$ and CAS# 104389-31-3. The analyzed sample (0.4 mg) had $M_w = 38,000$ (synthetic material), and the experimental conditions were similar to those for other polymers previously discussed (see Table 4.2.2). The resulting pyrogram is given in Figure 7.1.3, and the peak identification that was done using MS spectral library searches only is given in Table 7.1.4.

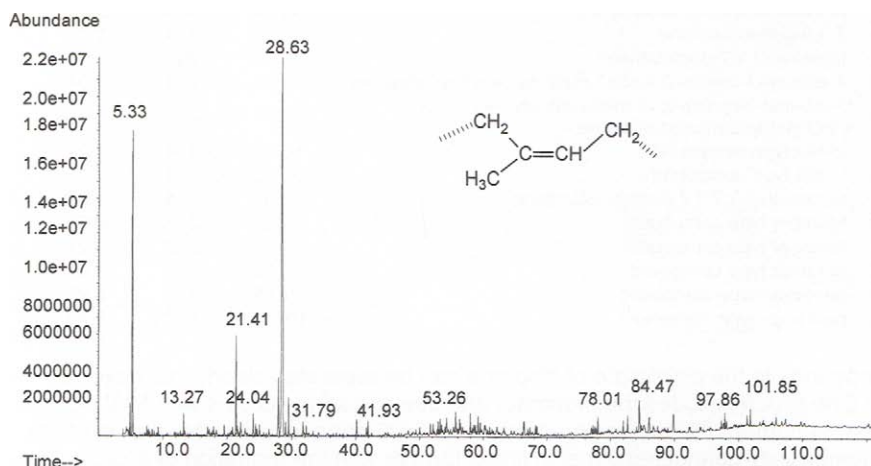


FIGURE 7.1.3. Pyrogram from a Py-GC/MS analysis of polyisoprene (*cis*), $M_w = 38,000$. Pyrolysis done on 0.4 mg material at 600°C in He, with the separation on a Carbowax type column.

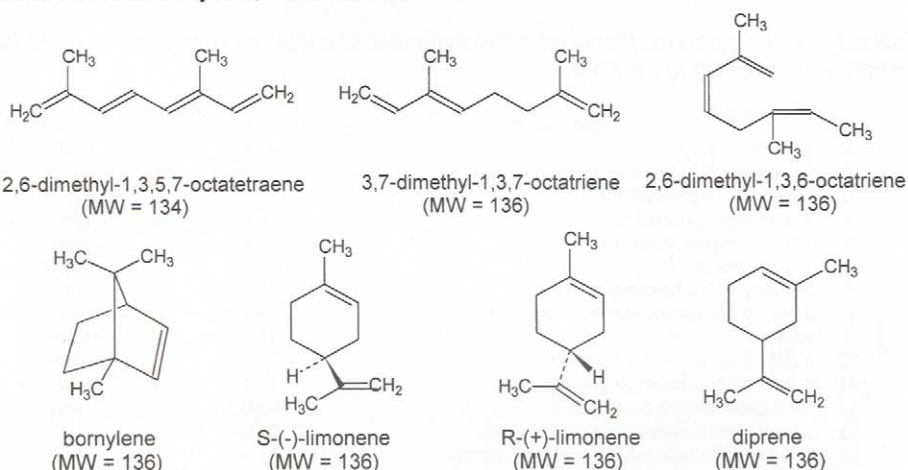
TABLE 7.1.4. Compounds identified in the pyrogram of a polyisoprene (*cis*), $M_w = 38,000$ sample as shown in Figure 7.1.3.

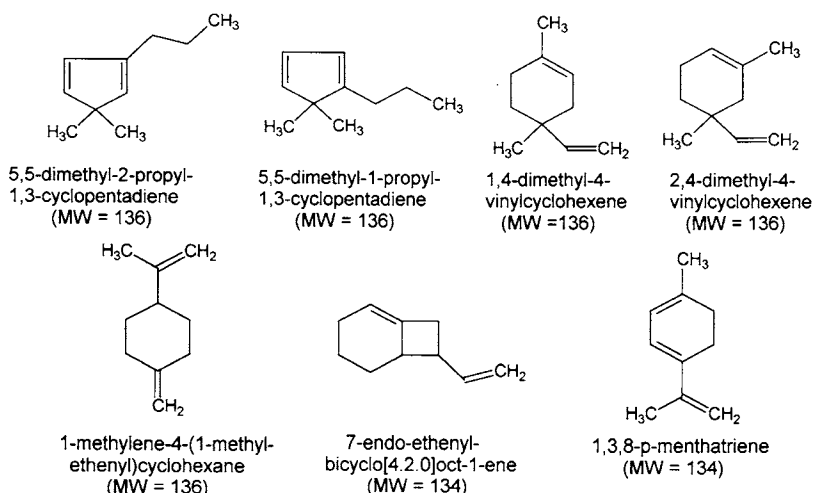
Peak	Compound	Ret. Time	MW	Area %
1	2-methyl-1-butene	4.99	70	1.37
2	2-methyl-1,3-butadiene (monomer)	5.33	58	17.87
3	2-methyl-1,3-pentadiene	7.55	82	trace
4	4,4-dimethylcyclopentene	9.31	96	trace
5	1,3-dimethylcyclohexene	11.41	110	trace
6	1,3,5-heptatriene	12.71	94	trace
7	3-methyl-1,3,5-hexatriene	13.27	94	1.06
8	3,3-dimethyl-6-methylenecyclohexene	16.95	122	trace
9	toluene	17.95	92	trace
10	2,3,6-trimethyl-1,4,6-heptatriene	19.55	136	trace
11	4-ethenyl-1,4-dimethylcyclohexene	21.41	136	6.02
12	<i>cis</i> -2,6-dimethyl-2,6-octadiene	22.08	138	trace
13	3-methyl-6-(1-methylethyl)cyclohexene	24.04	138	1.39
14	5,5-dimethyl-2-propyl-1,3-cyclopentadiene	27.94	136	3.98
15	limonene	28.63	136	49.43
16	1-methylene-4-(1-methylethenyl)cyclohexane	29.39	136	trace
17	5,5-dimethyl-1-propyl-1,3-cyclopentadiene	29.54	136	2.06
18	(E)-2,6-dimethyl-1,3,5,7-octatetraene	30.36	134	trace

TABLE 7.1.4 (continued). Compounds identified in the pyrogram of a polyisoprene (cis), $M_w = 38,000$ sample as shown in Figure 7.1.3.

Peak	Compound	Ret. Time	MW	Area %
19	3,7-dimethyl-1,3,7-octatriene	31.79	136	0.87
20	7-endoethenyl-bicyclo[4.2.0]oct-1-ene	32.25	134	trace
21	3,7-dimethyl-1,3,7-octatriene	40.14	136	0.94
22	2,6-dimethyl-2,4,6-octatriene	41.65	136	trace
23	1,3,8-p-menthatriene	41.93	134	0.76
24	trimethyl-?,?,?-dodecatriene	53.26	206	0.86
25	1-ethenyl-1-methyl-2,4-bis(1-methylethenyl)cyclohexane	54.26	204	1.04
26	1-ethenyl-1-methyl-2-(1-methylethenyl)-4-(1-methylethylidene)cyclohexane	55.67	204	1.37
27	trimer type compound	57.98	204	1.21
28	trimer type compound	59.22	204	1.23
29	tetramethyl-?,?,?-hexadecatetraene	78.01	274	0.92
30	tetramer type compound	82.67	272	0.90
31	tetramer type compound	84.47	272	3.21
32	tetramer type compound	86.08	272	1.81
33	pentamer type compound	97.86	342	0.80
34	pentamer type compound	101.85	342	0.92

The compounds in the pyrolysate of isoprene can be separated clearly into several groups. One group includes the monomer and other small molecules with MW close to that of the monomer. The other group contains the dimer and molecules derived from two monomer units connected either in linear form or with the formation of a cycle. There are more groups related to three monomer units, four monomer units, etc. Examples of the pyrolysate components with two monomer units, some of them indicated in Table 7.1.4 and having MW = 134 or MW = 136 depending on the number of double bonds or cycles, are shown below:





The number of compounds related to the trimer of the 2-methyl-1,3-butadiene, with MW = 202, MW = 204, or MW = 206 depending on the number of double bonds or cycles, is very high. All these compounds elute in the same area of the chromatogram shown in Figure 7.1.4, which displays the region between 44.0 min. to 70.0 min. from the whole chromatogram given in Figure 7.1.3. The abundance range for the chromatogram from Figure 7.1.4 is about 15 times smaller than the range for that from Figure 7.1.3.

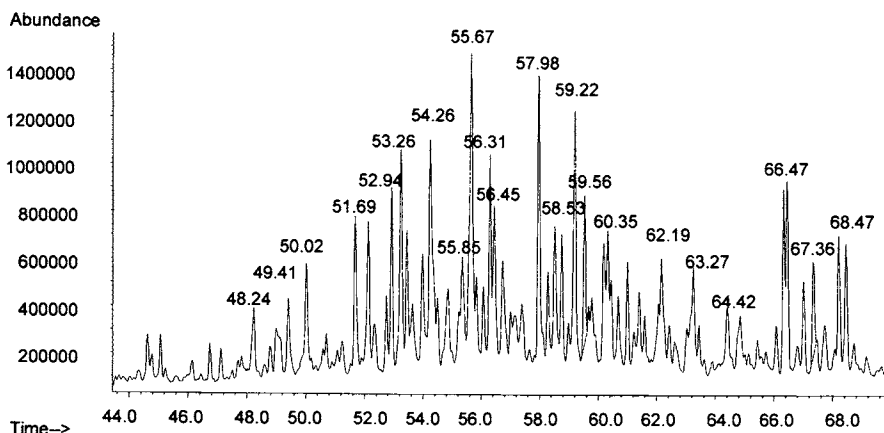


FIGURE 7.1.4. Time window between 44.0 min. and 70.0 min. for the pyrogram given in Figure 7.1.3. This window shows the trimer type compounds generated during pyrolysis of polyisoprene (cis).

A time window from 78.0 min. to 92.0 min. showing the tetramer type compounds generated in pyrolysis of polyisoprene is shown in Figure 7.1.5. The abundance range for the chromatogram in Figure 7.1.5 is about 10 times smaller than the range for the chromatogram from Figure 7.1.3.

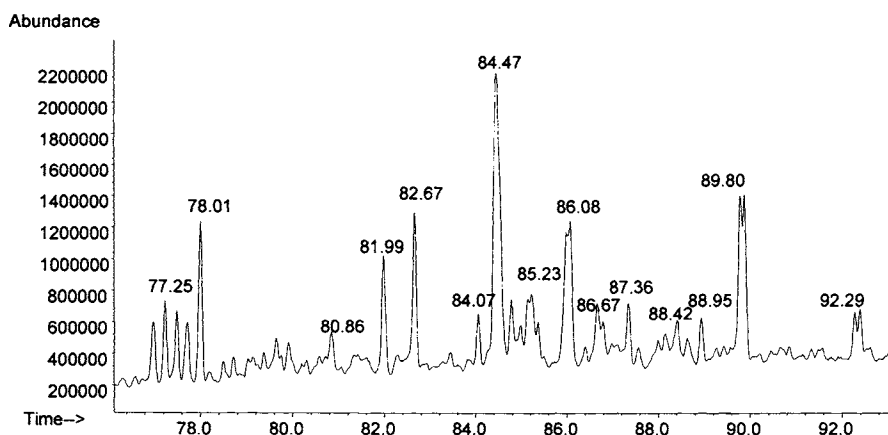
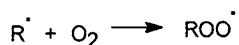


FIGURE 7.1.5. Time window between 76.0 min. and 93.0 min. for the pyrogram given in Figure 7.1.3. This window shows the tetramer type compounds generated during pyrolysis of polyisoprene (*cis*).

Pyrolysis of polyisoprene takes place very similarly to that of polybutadiene. The β -chain scission (to the double bond) is the dominant initiation process, and the bond dissociation energy was estimated to be about 61.5–63 kcal mol⁻¹. The cleavage of the carbon chain backbone has as the final result the elimination of some monomer, linear and cyclic dimers, trimers, etc. The yield of monomer depends on the heating conditions, degree of polymerization, etc. Table 2.1.1 indicates the formation of up to 58% monomer from natural rubber pyrolysis, while Table 7.1.4 shows only about 18% conversion. Some aspects regarding the thermal decomposition mechanism of polyisoprene were discussed in Section 2.1.

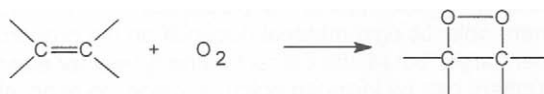
Synthetic polyisoprene displays during pyrolysis an identical behavior with natural rubber. Pyrolysis of natural rubber, which is pure *cis*-polyisoprene, is reported frequently in literature [29–35]. A review of the subject can be found in [36].

Pyrolysis of synthetic polyisoprene in the presence of oxygen also is expected to be identical to that of natural rubber. Thermal oxidation of natural rubber is assumed always to be associated with scission, although photo-oxidation at low temperature may involve peroxide formation without scission. The effect of oxygen is to increase the reaction rate of scission and therefore to decrease the temperature where the scission starts. The oxidation may take place after the initial formation of a free radical that reacts with oxygen:

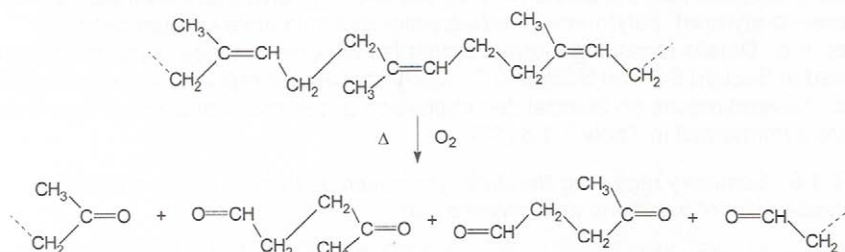


The peroxide radical can go to a product by abstraction of a hydrogen and generate an acid and another radical. Commonly, acetic acid and also formic acid are formed in considerable amounts during oxidative pyrolysis. The previous mechanism can

probably explain the formation of these small molecules. The oxygen (singlet oxygen) also may react with the double bond forming a dioxetane intermediate:



The O-O bond is weak (30–50 kcal/mol) and may break with the formation of aldehydes or ketones. One main product in scission/oxidation of rubber is levulinolaldehyde, and formally its formation can be written as:



The main oxidation products reported for the oxidative pyrolysis of natural rubber are given in Table 7.1.5 [36].

TABLE 7.1.5. Oxidative pyrolysis products of natural rubber.

Compound	Formula	MW
water	H ₂ O	18
carbon monoxide	CO	28
carbon dioxide	CO ₂	44
formic acid	CH ₂ O ₂	46
methanol	CH ₄ O	32
acetaldehyde	C ₂ H ₄ O	44
acetic acid	C ₂ H ₄ O ₂	60
methyl formate	C ₂ H ₄ O ₂	60
ethanol	C ₂ H ₆ O	46
pyruvaldehyde	C ₃ H ₄ O ₂	72
acetone	C ₃ H ₆ O	58
propionaldehyde	C ₃ H ₆ O	58
methyl acetate	C ₃ H ₆ O ₂	74
butenone	C ₄ H ₆ O	70
2-methylpropenaldehyde	C ₄ H ₆ O	70
butanone	C ₄ H ₈ O	72
2-methylfuran	C ₅ H ₆ O	82
β-angelica lactone (5-methyl-2(5H)-furanone)	C ₅ H ₆ O ₂	98
levulinolaldehyde	C ₅ H ₈ O ₂	100
γ-valerolactone	C ₅ H ₈ O ₂	100
hexanedione	C ₆ H ₈ O ₂	112

The pyrolysis products of synthetic *cis*-polyisoprene in an oxidative pyrolysis are very likely identical with those shown in Table 7.1.5.

- Copolymers of 1,3-butadiene and of isoprene

Butadiene is used in very large quantities in copolymers used as synthetic rubber or as thermoplastic materials with good mechanical properties. The characteristics of being an elastomer or a thermoplastic rigid material depends on the proportion of butadiene used in the copolymer, larger butadiene content being typical for elastomers. In the group of synthetic rubbers can be included poly(butadiene-co-acrylonitrile) known as nitrile butadiene rubber or NBR, poly(styrene-co-butadiene) or SBR, poly(acrylonitrile-co-butadiene-co-isoprene), poly(1,3-butadiene-co-1,3-pentadiene), poly(1,3-butadiene-co-1,1-dichloroethene-co-styrene), poly(styrene-*block*-isoprene), etc. In the group of rigid thermoplastic materials can be included poly(methyl methacrylate-co-butadiene), poly(methyl methacrylate-co-acrylonitrile-co-butadiene), poly(methyl methacrylate-co-butadiene-co-styrene), poly(methyl methacrylate-co-acrylonitrile-co-butadiene-co-styrene), etc. Details regarding thermal properties of some of these copolymers were discussed in Section 6.2 and Section 6.7. Many studies are reported in literature [37–41], etc. Several results on thermal decomposition of common copolymers from this class are summarized in Table 7.1.6 [19].

TABLE 7.1.6. Summary regarding literature information on thermal decomposition of some copolymers of butadiene and isoprene [19].

Polymer	Temp. °C	Results	Ref.
poly(butadiene)- <i>blend</i> -poly(styrene) (0-100 wt. %)	ambient to 500	volatile products as for individual polymers	42
poly(butadiene-co-acrylonitrile) (70/30)	310–400	14.5% of products are volatile at 25°C, consisting of saturated hydrocarbons	43
poly(butadiene-co-acrylonitrile) 25-100 mol % butadiene	350–400	main product is structurally modified chain fragments; ammonia and hydrogen cyanide increasing with acrylonitrile content to approximately 4% each by weight of copolymer containing mole 75% acrylonitrile; traces of hydrogen and hydrocarbons up to C ₇	44
poly(butadiene-co-acrylonitrile)	-	ethenylcyclohexene, acrylonitrile, etc.	45
poly(butadiene-co-isoprene)	600	the composition and sequence distribution of monomeric units has been determined	46, 47
poly(butadiene-co-styrene)	-	weight loss at 261-309°C for the copolymer with 23-40% styrene	48
poly(butadiene-co-styrene) (75/25)	327–430	11.8% of products are volatile at 25°C; 1.9% butadiene with other saturated and unsaturated hydrocarbons	27, 43
poly(isoprene)- <i>blend</i> -poly(styrene) (4/1 to 1/4, w/w)	ambient to 500	styrene, isoprene, dipentene larger chain fragments of both polymers, traces of ethylene, ethane, and propane	49
poly(isopropenyl-cyclohexane-co- α -methylstyrene) (92/8 and 33/67)	400–900	methylenecyclohexane and/or methyl-1-cyclohexane, benzene, toluene, isopropenylcyclohexane, ethylbenzene (92/8 only), decalin (92/8 only), cumene (33/67 only), α -methylstyrene, styrene, (33/67 only), pentadienylcyclohexane (92/8 only), indene and methyleneindene (33/67 only), naphthalene, dicyclohexylhexadiene (92/8 only). The following from the 33/67 copolymer only: 2-methylnaphthalene, 1-methylnaphthalene, biphenyl, methylstilbene, α -methylstilbene, anthracene/phenanthrene, dihydropyrene	50

Examples of Py-GC/MS results on copolymers of butadiene were already given in Section 6.2 for polystyrene-*block*-polybutadiene (Figure 6.2.10) and in Section 6.7 for poly(acrylonitrile-co-butadiene) (Figure 6.7.25) and for poly(acrylonitrile-co-butadiene-co-styrene) (Figure 6.7.26).

The results for the pyrolysis of a polyisoprene-graft-maleic anhydride sample with $M_w = 25,000$, CAS# 139948-75-7, is shown in Figure 7.1.6. The pyrolysis was done at 600°C in He with separation of a Carbowax column and MS detection, similarly to other polymers discussed in this book (see also Table 4.2.2). The peak identification for the chromatogram shown in Figure 7.1.6 was done using MS spectral library searches only and is given in Table 7.1.7.

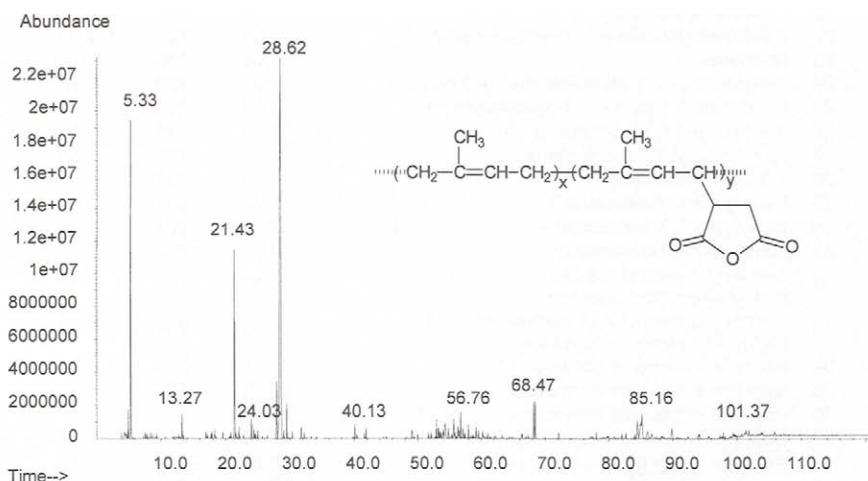


FIGURE 7.1.6. Result for a Py-GC/MS analysis of polyisoprene-graft-maleic anhydride with $M_w = 25,000$. Pyrolysis done at 600°C in He, with the separation on a Carbowax type column.

TABLE 7.1.7. Compounds identified in the pyrogram of polyisoprene-graft-maleic anhydride with $M_w = 25,000$, as shown in Figure 7.1.6.

Peak	Compound	Ret. time	MW	Area
1	propene	4.35	42	trace
2	2-methyl-1-propene	4.65	56	trace
3	2-methyl-1-butene	4.99	70	1.09
4	2-methyl-1,3-butadiene	5.33	68	15.16
5	2-methyl-1,3-pentadiene	7.56	82	trace
6	2,4-hexadiene	7.81	82	trace
7	1,3,5-hexatriene	8.46	80	trace
8	4,4-dimethylcyclopentene	9.33	96	trace
9	1,3-dimethylcyclohexene	11.41	110	trace
10	3-methyl-1,3,5-hexatriene	13.27	94	1.04
11	3,3-dimethyl-6-methylenecyclohexene	16.97	122	0.34
12	2,3-dimethylcyclohexa-1,3-diene	17.74	108	trace
13	toluene	17.90	92	0.51
14	1,6-dimethylhepta-1,3,5-triene	18.35	122	0.48
15	2,3,6-trimethyl-1,4,6-heptatriene	19.56	136	trace
16	4-ethenyl-1,4-dimethylcyclohexene	21.43	136	10.23
17	cis-2,6-dimethyl-2,6-octadiene	22.10	138	0.52

TABLE 7.1.7 (continued). Compounds identified in the pyrogram of polyisoprene-graft-maleic anhydride with $M_w = 25,000$, as shown in Figure 7.1.6.

Peak	Compound	Ret. time	MW	Area
18	3-methyl-6-(1-methylethyl)cyclohexene	24.03	138	0.82
19	1,4-dimethylbenzene	24.43	106	0.56
20	5,5-dimethyl-3-isopropenylcyclopentene	24.63	136	trace
21	2-methyl-6-methylene-1,7-octadiene	25.01	136	0.29
22	5,5-dimethyl-2-propyl-1,3-cyclopentadiene	27.96	136	2.92
23	limonene	28.62	136	42.35
24	1-methylene-4-(1-methylethenyl)cyclohexane	29.05	136	0.26
25	5,5-dimethyl-1-propyl-1,3-cyclopentadiene	29.54	136	1.41
26	3,7-dimethyl-1,3,7-octatriene	31.79	136	0.50
27	3,-7-dimethyl-1,3,7-octatriene	40.13	136	0.54
28	1,3,8-p-methatriene	41.93	134	0.39
29	trans-gamma-bisabolene ?	52.94	204	0.80
30	trimethyl-?,?,?-dodecatriene	53.25	204	0.71
31	trimethyl-?,?,?-dodecatriene	54.01	204	0.62
32	1-ethenyl-1-methyl-2,4-bis(1-methylethenyl)cyclohexane	54.30	204	1.32
33	1-ethenyl-1-methyl-2-(1-methylethenyl)-4-(1-methylethylidene)cyclohexane	55.66	204	1.50
34	isoprene trimer type compound	56.31	204	0.84
35	isoprene trimer type compound	56.76	204	1.22
36	isoprene trimer type compound	57.13	204	0.57
37	isoprene trimer type compound	57.98	204	0.56
38	isoprene trimer type compound	59.20	204	0.59
39	isoprene trimer type compound	59.55	204	0.37
40	isoprene trimer type compound	68.22	204	1.59
41	isoprene trimer type compound	68.47	204	1.55
42	isoprene tetramer type compound	84.45	272	1.54
43	isoprene tetramer type compound	85.16	272	3.75
44	isoprene tetramer type compound	86.02	272	0.72
45	isoprene tetramer type compound	89.82	272	0.97
46	isoprene pentamer type compound	101.37	342	0.96
47	isoprene pentamer type compound	101.85	342	0.40

The comparison of the pyrogram of polyisoprene-graft-maleic anhydride with that of polyisoprene shows no significant difference. Neither 2,5-furandione nor dihydro-2,5-furandione were detected in the pyrogram of polyisoprene-graft-maleic anhydride. The same absence was noticed for other *graft* copolymers of maleic anhydride, such as for poly(ethylene-graft-maleic anhydride) (see Section 6.1).

- Polyacetylene and other unsaturated polyhydrocarbons

Polyacetylene contains conjugated double bonds in a linear structure [51–54], which leads to special electrical conductivity properties. For this reason, polyacetylene and some other related polymers have applications in the optical and electronic industries. Polyacetylene synthesized at relatively low temperature seems to have a *cis*-conformation, with two possible *cis*-forms indicated as *cis-transoid*, and *trans-cisoid*, as shown below:



The heating of the polymer at about 150° C leads to a *trans* conformation [55], which is highly conducting.

A number of other unsaturated polyhydrocarbons have practical applications. These include poly(phenyl acetylene) and poly((E,E)-[6.2]paracyclophane-1,5-diene), which have been studied as photoconducting polymers. The thermal decomposition of polyacetylenes and of poly((E,E)-[6.2]paracyclophane-1,5-diene) generates fragments summarized in Table 7.1.8 [19].

TABLE 7.1.8. Summary regarding thermal decomposition of polyacetylene and of poly((E,E)-[6.2]paracyclophane-1,5-diene) [19].

Compound	Temp. °C	Results	Ref.
poly((E,E)-[6.2]-paracyclophane-1,5-diene)	460, 515, 620	primary product is monomer; in addition, a series of secondary products based on ring-opened monomer are formed by H-abstraction; also detected: toluene (not 460° C) and p-xylene	56
poly(phenyl acetylene)	325	decomposes with hydrogen migration and crosslinking reactions	57
poly(phenyl acetylene)	420	benzene	57
polyacetylene	650	methane (0.87 moles relative to benzene = 1), ethylene (0.47), ethane (0.26), propylene (0.27), propane (0.047), 1,3-butadiene (0.19), cyclopentadiene (0.086), cyclopentene (0.063), benzene (1.0), toluene (0.18), m-xylene (0.091), p-xylene (0.015), styrene (0.041), o-xylene (0.013), methylstyrene (0.010), trans-β-methylstyrene (0.011), indane (0.0074), indene (0.036), methylindene (0.0072), naphthalene (0.052), 2-methylnaphthalene (0.015), 1-methylnaphthalene (0.018), biphenyl (0.0091), fluorene (1.0), anthracene (0.005)	58

Several results regarding the pyrolysis of poly(*p*-phenylene-ethynylenes), which contain acetylene units connected with substituted phenylene in their backbone, are further discussed in Section 8.1.

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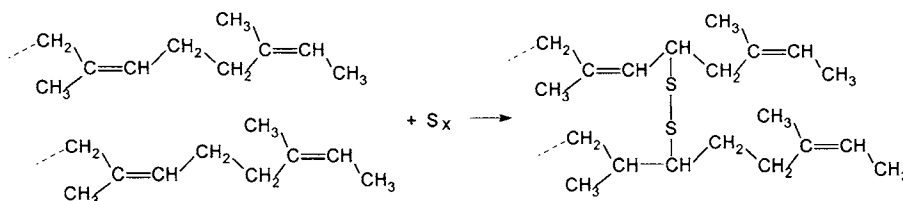
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7.2 VULCANIZED UNSATURATED POLYHYDROCARBONS

- General aspects

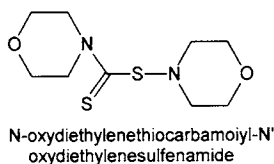
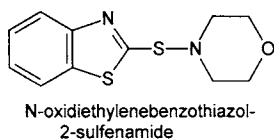
Vulcanization is an industrial process applied to various polymers from the class of unsaturated polyhydrocarbons. The major practical use of vulcanized elastomers is the tire industry. Tires are made from various polymer blends, including natural rubber, typically between 20 and 50%. The other polymers used in various blends that can be vulcanized include copolymers such as poly(styrene-co-1,3-butadiene) or SBR, poly(acrylonitrile-co-1,3-butadiene-co-styrene) or ABS, poly(isobutylene-co-isoprene), poly(ethylene-co-propylene-co-1,4-hexadiene), etc.

The common vulcanization process (not for chloroprene) consists of a chemical reaction of sulfur (0.5–5% wt.) with the polymer containing double bonds in the backbone. The reaction takes place at 130–145° C and may require mechanical mixing. The reaction for polyisoprene can be written schematically as follows:



The final product may contain a single sulfur atom bridge, sulfur in cyclic or pendant groups, or may contain polysulfide bridges between the polymer chains. The vulcanization introducing sulfur in the polymer also can be done at room temperature with S_2Cl_2 .

Besides sulfur, during the vulcanization process other chemical compounds are commonly added. One group of such compounds consists of *vulcanization accelerators*. Substances such as diphenylguanidine, mercaptobenzothiazole, tetramethythyuram disulfide, N-oxydiethylene-2-benzothiazolylsulfenamide, N-oxydiethylenethiocarbamoyl-N'-oxydiethylenesulfenamide, cyclohexylbenzothiazolylsulfenamide, etc. are utilized for this purpose. The structures of two sulfenamide accelerators are shown below:



Besides accelerators, other additives are used, including antioxidants, activators, solubilizers, plasticizers, and fillers. Among the *antioxidants* more frequently used are N-phenyl-β-naphthylamine, 2,6-di-*tert*-butyl-4-methyl-1-hydroxybenzene (BHT), N-

isopropyl-N'-phenyl-p-phenylenediamine, N-(1,3-dimethylbutyl)-N'-p-phenylenediamine, and poly-(2,2,4-trimethyl-1,2-dihydroquinoline). Common *activators* include metallic oxides, salts of calcium, zinc, or magnesium, etc. They work together with the accelerators to promote the vulcanization process. The solubilizers are compounds that enhance the solubility of various vulcanization components, and stearic acid salts are commonly used for this purpose. For *plasticizer agents* stearic acid, other long chain fatty acids, waxes, long chain hydrocarbons, etc. are used. The *fillers* are typically carbon black or mineral oxides (ZnO, silica), which are added to modify the mechanical properties of rubber.

Nonsulfur vulcanization has the same purpose as sulfur vulcanization and can be done using peroxides, quinones, azo compounds, or compounds that react similarly to sulfur such as selenium. However, nonsulfur vulcanization has lower practical importance. Commonly, chloroprene is vulcanized with nonsulfur compounds such as metal oxides (ZnO or MgO).

Pyrolysis of vulcanized natural rubber or polyisoprene generates the same compounds as natural rubber [1-4] and in addition some H_2S , SO_2 , CH_3SH . When additives are used during the vulcanization process, either intact molecules such as benzothiazole or fragments of these additives may be seen in the pyrograms. Py-MS results can be well correlated with the crosslinking density [5, 6]. For establishing this correlation, standards with different levels of vulcanization must be pyrolyzed, and the data processed using multivariate analysis.

Pyrolysis of vulcanized rubbers on industrial scale is a common operation in processing used tires. When shredded scrap tires are pyrolyzed between 450 and 600° C, they generate char (37–38 wt.%), oils (53–58 wt.%), and gases (4–9 wt.%) [7–9]. The gases are composed mainly of H_2 , CH_4 , C_4H_6 , CO, CO_2 . Other aliphatic hydrocarbons also were detected in the gases. The oils contain a mixture of hydrocarbons, and DL-limonene as a main component. Some aromatic hydrocarbons and also traces of polycyclic aromatic hydrocarbons (PAH) were detected in the pyrolysis oils. The level of PAHs in tire pyrolysate is relatively high. Compounds such as benzo[b]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, and dibenz[a,c]anthracene were not reported, although they are likely to be present at levels below 1–2 ppm (see Section 5.3) [9].

One of the applications of pyrolytic techniques in the study of rubber vulcanisates is the evaluation of crosslinking density [10, 11]. Pyrolytic data can be correlated with total crosslinking density. Pyrolysis results can be used based on the generation of individual compounds or using the whole set of results. An excellent correlation has been obtained, for example, between the crosslinking density and a canonical variate function obtained from the whole pyrolysis data set [5]. The results from such a study are illustrated in Figure 7.2.1.

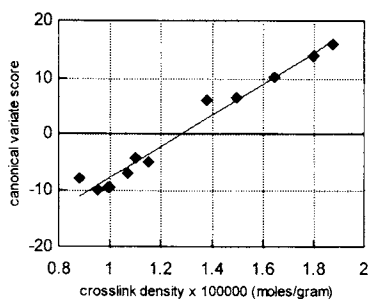


FIGURE 7.2.1. The correlation between crosslinking density of vulcanized rubber and the canonical variate score.

Similar results were obtained when the crosslinking values were correlated to the ratio of the peak areas or of peak heights of dipentene and 3-methyl-1,3-pentadiene detected in the vulcanized rubber pyrolysates [2]. Other studies using pyrolysis for the characterization of vulcanized rubbers (natural and synthetic) are reported in literature (see e.g. [12]).

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7.3 HALOGENATED UNSATURATED POLYHYDROCARBONS

- General aspects

Similar to the case of the polymers with saturated carbon chain backbone, different substitutions are possible to the backbone of the unsaturated macromolecules. One common substitution is with halogens. Chloroprene (also known as neoprene) is formed from the polymerization of 2-chloro-1,3-butadiene and probably is the most widely used polymer from this class. It has rubber-like properties and is known for its better oil

resistance compared to natural rubber. Chlorinated polymers having a backbone made by an unsaturated carbon chain also can be obtained by the incomplete chlorination of certain unsaturated polyhydrocarbons such as natural rubber (stereospecific *cis*-polyisoprene). Chloroprene can be vulcanized, but nonsulfur vulcanization usually is applied.

- Poly(2-chloro-1,3-butadiene) and other halogenated unsaturated polyhydrocarbons

Poly(2-chloro-1,3-butadiene) or polychloroprene, $(-\text{CH}_2\text{C}(\text{Cl})=\text{CHCH}_2-)_n$, CAS# 9010-98-4, is a polymer widely used in practice, for example in automotive industry for the fabrication of belts, gaskets, electrical cables covering, etc. (mainly in vulcanized form). The older procedure for chloroprene preparation starts with acetylene, which is subject to catalytic dimerization followed by addition of HCl to the vinylacetylene molecule. Newer processes start with butadiene, which is chlorinated to 1,4-dichlorobutene, followed by dehydrochlorination. The polymer is typically obtained by coordination or anionic polymerization in emulsion, leading to *trans*-1,4-form. Polychloroprene thermal stability is not very good, the polymer starting to decompose at about 170° C. The weight loss takes place slowly around 230° C and accelerates in the range 275–375° C with elimination of HCl and formation of carbon residue (char). The thermal degradation for commercial neoprenes starts with an initial weight loss (4%) at 265–280°, continuing with a fast weight loss at 380°, leaving a carbonaceous residue at 550° (21–23%) [1]. Vulcanized polychloroprene also has three stages of volatilization [2]. Polychloroprene vulcanization is usually different from that of other elastomers, and it is done by heat in the presence of oxides such as ZnO or MgO. Therefore the vulcanisates of polychloroprene do not necessarily show by pyrolysis the presence of sulfur. On the other hand, some types of polymerization are done in the presence of sulfur compounds such as tetraethylthiuram, which introduces some sulfur crosslinking in the polymer.

The presence of oxygen accelerates the thermal decomposition [3]. Decomposition at high temperatures yields CO₂, H₂O, and HCl [4]. Some other reports regarding polychloroprene thermal decomposition indicate formation of hydrogen chloride at 377° C [5], 2% of monomer, 70% of the chlorine released as HCl [6], for pyrolysis between 170° C and 400° C [7], and for pyrolysis between 400° C and 500° C formation of HCl, methane, ethylene, propylene (trace) [7]. Other pyrolysis studies also were reported [8–11].

Flash pyrolysis in He at 600° C of polychloroprene is dominated by the presence of the dimer of 2-chloro-1,3-butadiene and that of monomer as shown in the pyrogram given in Figure 7.3.1. Table 7.3.1 shows the peak identification obtained by MS library searches. The pyrogram was obtained in the same experimental conditions as those used for other examples in this book (see Table 4.2.2). The sample was made of polychloroprene 10% *cis*, 85% *trans*.

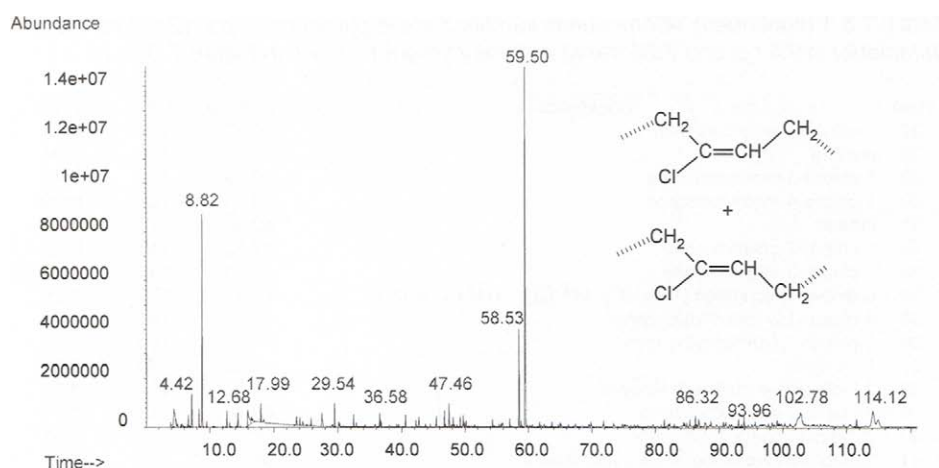


FIGURE 7.3.1. Pyrogram from a Py-GC/MS analysis of poly(2-chloro-1,3-butadiene) (10% cis and 85% trans). Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 7.3.1. Compounds identified in the pyrogram of poly(2-chloro-1,3-butadiene) (10% cis and 85% trans) with the pyrogram shown in Figure 7.3.1.

Peak	Compound	Ret. Time	MW	Area%
1	ethene	4.38	28	1.17
2	1-propene	4.44	42	0.41
3	1-butene	4.53	56	0.55
4	2-butene	4.63	56	1.07
5	1,3-butadiene	4.73	54	0.45
6	chloroethene	5.00	62	0.25
7	2-chloro-1-propene	5.46	76	trace
8	1,3-pentadiene	5.63	68	trace
9	1,4-pentadiene	5.79	68	trace
10	acetaldehyde	5.90	44	trace
11	1,3-cyclopentadiene	6.54	66	trace
12	1-chloro-2-butene	6.67	90	0.91
13	2-chloro-2-butene	7.21	90	2.18
14	3-chloro-2-methyl-1-propene	8.33	90	1.46
15	2-chloro-1,3-butadiene	8.82	88	14.68
16	benzene	12.68	78	1.40
17	1-chloro-cyclopentene	14.40	102	1.31
18	hydrochloric acid	15.97	36	3.95
19	toluene	17.99	92	1.76
20	ethylbenzene	23.56	106	trace
21	p-xylene	23.97	106	trace
22	o-xylene	24.63	106	trace
23	2-chloroethenyl-1,3-butadiene	25.82	114	trace
24	m-xylene	27.54	106	1.77
25	chlorobenzene	29.54	112	1.96
26	1-ethyl-2-methylbenzene	30.13	120	trace

TABLE 7.3.1 (continued). Compounds identified in the pyrogram of poly(2-chloro-1,3-butadiene) (10% *cis* and 85% *trans*) with the pyrogram shown in Figure 7.3.1.

Peak	Compound	Ret. Time	MW	Area%
27	1-ethyl-3-methylbenzene	30.33	120	trace
28	styrene	32.50	104	1.04
29	1-chloro-3-methylbenzene	36.59	126	1.44
30	1-chloro-4-methylbenzene	36.83	126	trace
31	indane	40.63	118	1.22
32	1-chloro-2-ethylbenzene	42.62	140	trace
33	1-chloro-3-ethylbenzene	42.73	140	1.33
34	unknown chlorinated [105(100), 141(62), 77(45) 176(33)]	45.47	176	1.28
35	4-chloro-1,2-dimethylbenzene	46.75	140	1.45
36	2-chloro-1,4-dimethylbenzene	47.46	140	2.93
37	1H-indene	48.10	116	0.88
38	2,3-dihydro-4-methyl-1H-indene	49.22	132	1.28
39	1-chloro-3-ethenylbenzene	49.71	138	1.76
40	2,6-dichloroocta-2,4,6-triene	57.07	176	0.61
41	1-chloro-5-(1-chloroethenyl)cyclohexene	58.53	176	8.72
42	1-chloro-4-(1-chloroethenyl)cyclohexene	58.84	176	trace
43	3,7-dichloroocta-1,4,6-triene (2-chlorobutadiene dimer)	59.50	176	36.49
44	naphthalene	63.69	128	trace
45	unknown chlorinated [89(100), 53(42), 91(38) 1141(23), ...231(9)]	86.32		1.39
46	unknown chlorinated [105(100), 115(62), 141(32), 53(31)...245(3)]	86.85		1.08
47	unknown chlorinated [71(100), 129(87), 127(82), 73(78)]	114.11		1.79

Except for the elimination of HCl, pyrolysis products of polychloroprene correspond rather well with those of isoprene. Besides the monomer and 3,7-dichloroocta-1,4,6-triene (which can be considered as a dimer of chloroprene), another compound found in appreciable levels in polychloroprene pyrolysate is 1-chloro-5-(1-chloroethenyl)-cyclohexene. This compound corresponds to diprene or 1-methyl-5-(1-methylvinyl)-cyclohex-1-ene in the pyrolysate of polyisoprene.

Results for some other halogenated unsaturated polyhydrocarbons were reported in literature. For example, poly(perfluoro-4-chloro-1,6-heptadiene) upon heating between 320° C and 400° C is reported to completely volatilize [12]. Also, reports on chlorinated rubber show that by heating from ambient to 500° C, it generates almost quantitatively HCl, and in the later stages of reaction CH₄, C₂H₄, and H₂ [13].

Pyrolysis of chlorinated unsaturated polyhydrocarbons is in some respects similar to that of the parent polyhydrocarbon, and in some others similar to halogenated saturated hydrocarbon type polymers. The elimination of the hydrohalogenated acid takes place relatively easily, and the polymers from this class are not resistant to heating. In practice, additives that enhance the resistance to heating frequently are added. Since the elimination of the acid seems to accelerate thermal decomposition, similarly to the case of PVC, metallic oxides that scavenge the acid increase the resistance to heating. The main pyrolysis products of each polymer are not modified by the addition of these additives.

- Copolymers of various other derivatives of butadiene and isoprene

Results regarding thermal behavior of a few other copolymers using as comonomers butadiene or isoprene derivatives are reported in literature. For example, thermal decomposition of poly(chloroprene)-*blend*-poly(methyl-methacrylate) has been studied starting at ambient temperature to 500° C. Upon heating the polymer generates methyl methacrylate, HCl, CO₂, CO, methyl chloride, and methanol [14]. Another material evaluated is chlorinated rubber-*blend*-poly(vinyl chloride). The heating of this blend in the range 160° C to 350° C generates HCl and a residue [15].

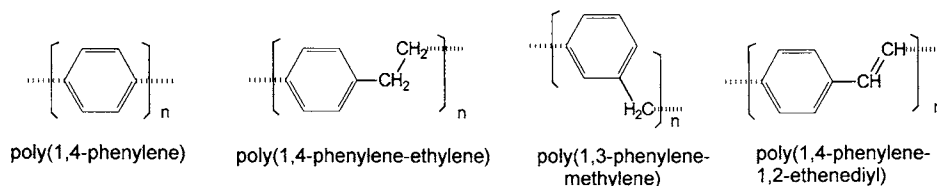
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CHAPTER 8

*Polymers with Aromatic Hydrocarbon Backbone***8.1 POLYHYDROCARBONS WITH AROMATIC RINGS IN THE MAIN CHAIN****- General aspects**

A significant number of polymers contain phenylene groups in their backbone. Most of these polymers also contain heteroatoms or heteroatom groups in the backbone and are discussed with other classes of polymers. However, there are some polymers with a carbon backbone that have only aromatic rings, alternating aromatic rings and aliphatic groups, or aromatic rings and unsaturated carbon chain fragments in their backbone. Examples of such polymers are poly(1,4-phenylene), poly(1,4-phenylene-ethylene), poly(1,3-phenylene-methylene), and poly(p-phenylene vinylidene), which are shown below:



Polymers with more complicated structures, containing triple bonds in addition to the aromatic cycles in the backbone or having substituents on the aromatic ring, also are known and have specific applications.

Thermosetting phenolic *resins* form a separate class of polymers containing aromatic rings and aliphatic carbon groups in the polymeric network. These resins are formed from the reaction of phenol (or substituted phenols) with formaldehyde. The fully crosslinked macromolecule is insoluble and infusible. Other thermosetting resins are known in practice, some derived from the reaction of melamine or of urea with formaldehyde. Because these have a different chemical structure, containing nitrogen, they are included in a different class (see Section 15.3).

- Polyphenylene and poly(phenylene-alkylenes)

Polyphenylene, CAS# 26008-28-6, is a temperature resistant polymer with the decomposition temperature around 660° C (see Table 3.1.1). For this reason it has applications in heat resistant fabrics, electrical insulators, etc. The thermal decomposition products of the polymers in this group are formed by random scission of the bonds that are not involved in the aromatic rings. This leads in most cases to the formation of oligomers. If side groups are attached to the benzene rings, fragments from these groups typically are seen in the pyrograms. Some reported results for the thermal decomposition of the polymers in this group are summarized in Table 8.1.1 [1].

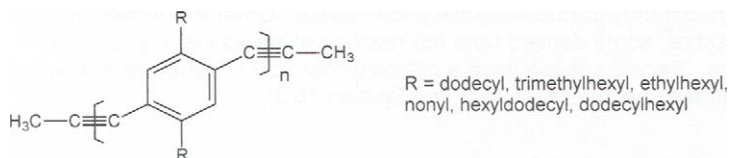
TABLE 8.1.1. Summary regarding literature reports on the thermal decomposition of polyphenylenes [1].

Polymer	Temp. °C	Results	Ref.
poly(1,3-phenylene-methylene)	386–416	7.4% of products are volatile at 25° C; 5.9% toluene, 1.4% benzene, 0.1% xylene	2, 3
poly(1,4-phenylene ethylene)	420–465	3.6% of products are volatile at 25° C and consist of 2.83% xylene, 0.29% toluene, 0.28% methylethylbenzene, 0.14% methylstyrene, 0.06% benzene, products nonvolatile at 25° C consist of dimeric to octameric fragments	2–4
poly(1,4-phenylene ethylene)	408–515	mainly chain fragments (dimer to pentamer); traces of H ₂ , monomer	5
poly(1,4-phenylene ethylene)	436–475	H ₂ , CH ₄ , C ₂ H ₄ , C ₂ H ₆ , toluene, p-xylylene, p-ethyltoluene, p-methyldibenzyl, 1,2-di-p-tolyethane, 4,4'-dimethylstilbene	6
poly(1,4-phenylene)	250–620	79% residue, 10% chain fragments, 11% volatiles comprising H ₂ , CH ₄ , H ₂ O, HCl (from the catalyst)	7
poly(1,4-phenylene)	600–800	oligomers, no benzene or biphenyl	8
poly(2-hydroxy-1,4-phenylene)	300–620	60% residue, 24% chain fragments, 16% volatiles comprising CO, CO ₂ H ₂ , CH ₄	7

- Other polymers with phenylene groups in the backbone

Other polymers containing phenylene groups in a carbon chain backbone include those with some unsaturated groups between the phenylene rings. Some of these polymers still have good stability upon heating, such as poly(1,4-phenylene-1,2-ethenediyl), CAS# 26009-24-5, which decomposes around 400° C [9]. Their use is, however, geared toward their special electricity conducting properties generated by the conjugated unsaturated groups and the aromatic rings. The compounds from this group also may have substituents on the aromatic ring [10].

Among the polymers containing aromatic rings and unsaturated hydrocarbon groups in the backbone are poly(phenylene-ethynylene)s (PPE). This type of polymer has been synthesized by alkyne metathesis of 1,4-dipropynylated benzenes [11] and has applications in optical and electronic industry. A comprehensive study on thermal decomposition of several poly(substituted p-phenylene-ethynylenes) is available [12]. The general formula for this group of polymers is the following:



As shown for the pyrolysis of poly(maleic anhydride-*alt*-1-octadecene) (see Section 6.8), when a long alkane chain is present in a polymer, the fragment alkanes and alkenes from the side chain generate large peaks in the pyrograms. The same effect is seen for the pyrolysis of PPEs, and a considerable number of peaks in the pyrograms of different substituted PPEs are identical, being generated from the fragmentation of the polymer side chains. However, some peaks are different and they can be used for the differentiation and identification of different polymers from this group.

References 8.1

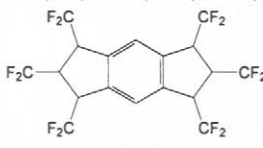
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8.2 HALOGENATED POLYHYDROCARBONS WITH AROMATIC RINGS IN THE BACKBONE

- General aspects

The polymers from this group show excellent thermal stability when they do not contain hydrogens, for example, when they are perfluorinated. Compounds having both hydrogen and a halogen (such as fluorine) eliminate the hydrohalogenated acid (HF, HCl, etc.) at lower temperatures. Some literature reports on thermal decomposition for this group of compounds are indicated in Table 8.2.1 [1].

TABLE 8.2.1. Summary regarding reports on the thermal decomposition of halogenated polyphenylenes [1].

Polymer	Temp. °C	Results	Ref.
poly(1,3-phenylene-hexafluorotri-methylene)	660 for 30 s	C_2F_4 (21.6% of original weight of polymer), HF (17), C_6H_6 (8.5%), $C_6H_5(CF_2)_3C_6H_5$ (7.9%), $C_6H_5(CF_2)_5C_6H_5$ (10.2%)  (13.9%)	2
poly(perfluoro- <i>m</i> -phenylene)	700	volatiles comprise SiF_4 (from silica vessel), CO_2 , with traces of C_6F_6 and C_6F_5H ; white sublimate on vessel walls when heated in a microfurnace, residue contains 1% fluorine	3
poly(perfluoro- <i>m</i> -phenylene) high MW (15000)	700	volatiles comprise SiF_4 (from silica vessel), CO_2 , with traces of C_6F_6 and C_6F_5H ; white sublimate on vessel walls; residue contains 1% fluorine	3
poly(perfluoro- <i>m</i> -phenylene) low MW (3700)	700	volatiles comprise SiF_4 (from silica vessel), CO_2 , with traces of C_6F_6 and C_6F_5H ; no white sublimate; residue contains 33-41% fluorine	3

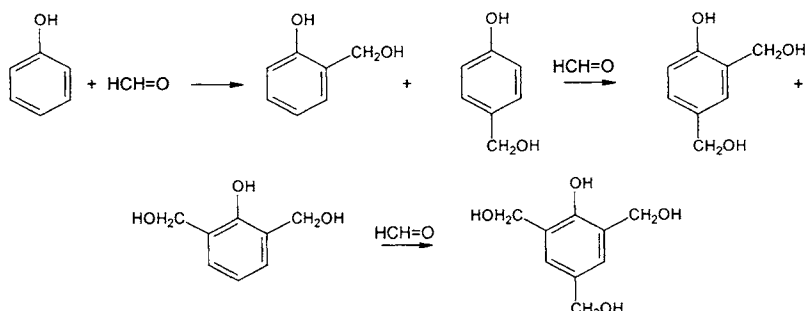
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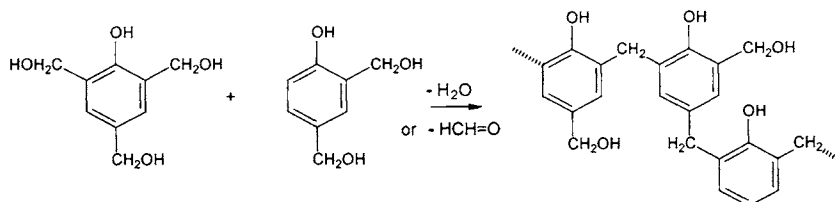
8.3 THERMOSETTING PHENOLIC RESINS AND RELATED POLYMERS

- General aspects

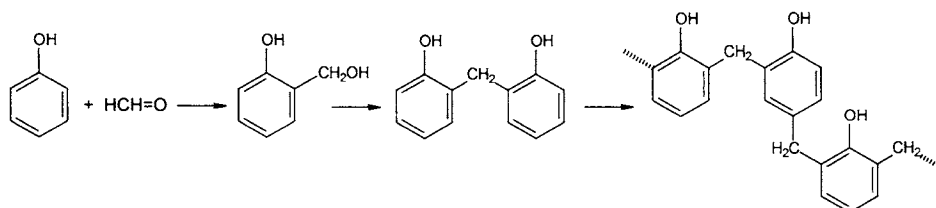
Thermosetting phenolic resins include a number of polymers, the most common being obtained from the condensation of phenol with formaldehyde. The OH group on the benzene ring increases the reactivity in the *o*- and *p*- positions leading to three reactive centers for the phenolic component, while formaldehyde acts as having two active centers that can lead to a fully crosslinked polymer. The process may take place in neutral or alkaline conditions when in the first stage of the reaction, compounds known as methylol derivatives are formed. The condensation of phenol with formaldehyde occurs randomly at *ortho*- or *para*- position of the phenol, as shown below:



The methylol derivatives under mild heating for a limited time further react forming fusible polymers that are not yet fully crosslinked, as shown below:

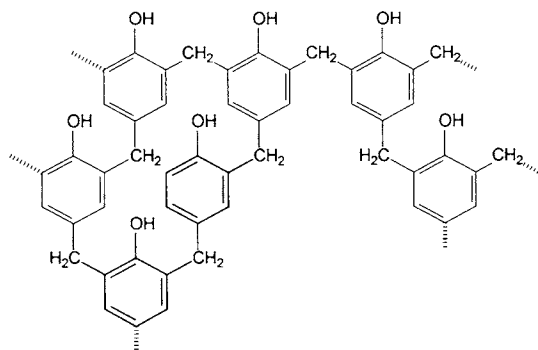


In acidic conditions, the reaction between phenol and formaldehyde is believed to occur with the formation of a linear polymer as follows:



Since the fully crosslinked macromolecule is insoluble and cannot be processed by molding, it is common in practice to synthesize first a polymer with a low degree of polymerization that can melt, followed by further crosslinking. This process is known in practice as formation of a two-stage resin (one-stage process is less frequently used). The two-stage resin can be obtained either using basic or acidic conditions. In basic conditions, the first stage must be done at low temperatures and with strictly controlled reaction times. Polymers with relatively low molecular weight and containing numerous $\text{-CH}_2\text{OH}$ groups attached to the benzene rings can be obtained (as previously shown). In the second stage, these polymers known as resols can be further crosslinked by heating, when more condensations are induced by the elimination of water.

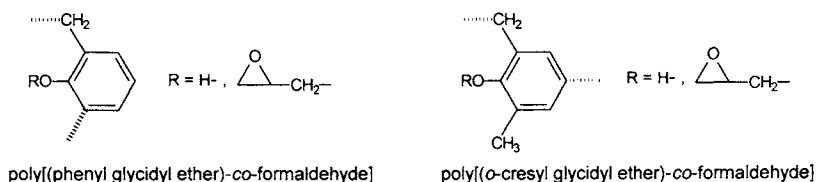
A different way to synthesize fusible polymers is to conduct the first stage in acidic conditions with the mole ratio of formaldehyde to phenol less than 1 and with mild heating. The linear polymer formed in this way is called novolac (or novolak). The novolac is further transformed into a crosslinked polymer by the addition of more formaldehyde and a basic catalyst. The process can be accomplished by adding during molding the novolac mixed with an appropriate amount of hexamethylene-tetramine. The decomposition of hexamethylenetetramine during heating generates formaldehyde and ammonia, which acts as a basic catalyst. The idealized structure of a crosslinked phenol-formaldehyde resin is shown below:



In the synthesis of this polymer in the presence of NaOH, long chain or highly branched molecules are obtained, depending on factors such as phenol to formaldehyde mole ratio, phenol to NaOH mole ratio, and the temperature and duration of the heating.

Other resins from this group may be obtained with the phenolic component with additional substituents on the benzene ring such as alkyl (methyl, dimethyl, butyl, *tert*-

octyl, nonyl), alkenyl (decapentatrienyl when using cardanol), etc. Phenolic resins with two -OH groups present on the benzene ring, like in resorcinol-formaldehyde resin, also are known. Instead of OH groups, ether groups also activate the ortho and para positions on the benzene ring. For example, glycidyl ethers were used as phenolic component, and these groups allow further crosslinking (curing) of the macromolecule. When the attached groups are glycidyl (epoxy propyl), these compounds are known as epoxynovolaks (or epoxynovolac). Typically these polymers also contain some free phenol groups. The idealized structures of two resins containing glycidyl ether attached to the benzene ring are shown below:



The polymers are initially obtained in linear form, being thermoplastic and soluble in different solvents. The heating of the polymer allows further crosslinking by the opening of the oxirane ring and formation of intermolecular bridges. These types of polymers are used as active components in some epoxy resins. Also, resins containing other aromatic moieties are known. Among these is, for example, naphthalene sulfonate formaldehyde resin, which can be used as a cement additive [1]. Also, thiophenol forms a condensation product with formaldehyde. However, the condensation with thiophenol occurs with a different mechanism than that of phenol, and sulfur atoms are included in the backbone of the polymer. For this reason, thiophenol/formaldehyde resin is discussed in Section 12.1.

Phenolic resins have many practical applications. They are widely used to make plywood for furniture and wall paneling when wood dust or wood chips are included as a filler. With paper or fabric phenol-formaldehyde resins form various laminates including those necessary for making boards for electronic circuits. Phenolic resins also are used to bind fiberglass, carbon fiber, and other reinforcing materials applied in aerospace industry. The binding of a filler can be done by different technological procedures, either starting with a solution of novolac that is used to soak the filler followed by heating, or in mixtures of resol or novolac with the filler that is thermoset in the desired shape of the final object. Phenolic resins also have applications in coating industry for high-temperature wire insulation, for making electrical battery separators, for use as structural adhesives, etc. The phenolic foams are used for heat insulators in buildings. Also, phenolic resins can be components of various copolymers and may be used as vulcanizing agents for rubbers.

Phenol-formaldehyde resins are relatively resistant to heat. They start decomposing at about 250° C still maintaining some mechanical resistance, the decomposition rate increasing significantly around 300° C. In an inert atmosphere at 750° C, phenol-formaldehyde resins form more than 50% char [2, 3]. The volatile materials consist of xylene (76%), traces of phenol, cresol, and benzene [4]. The heating in air above 300° C leads to the oxidation of the carbonaceous char and complete volatilization of the polymer [5]. More information regarding pyrolysis products of phenol-formaldehyde

resins can be found in a report on non-flaming burning of phenol-formaldehyde resin foam [6] and in other published materials on the use of pyrolytic techniques for the study of phenol-formaldehyde polycondensates [7–20].

A pyrogram for a crosslinked phenol-formaldehyde resin (made with a basic catalyst) was done similarly to that for other polymers exemplified in this book, at 600° C in He and with the separation on a Carbowax column and mass spectral detection (see Table 4.2.2). The peak identification for the chromatogram shown in Figure 8.3.1 is given in Table 8.3.1.

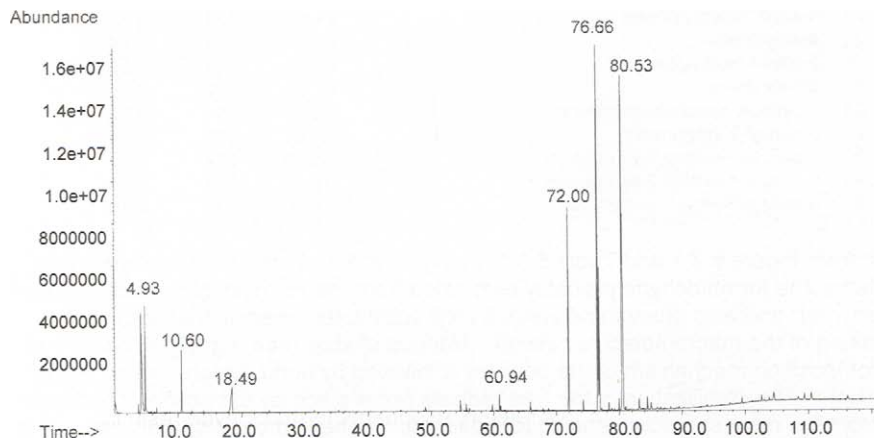


FIGURE 8.3.1. Pyrogram of a crosslinked phenol-formaldehyde resin sample. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 8.3.1. Compounds identified in the pyrogram of a crosslinked phenol-formaldehyde resin sample shown in Figure 8.3.1.

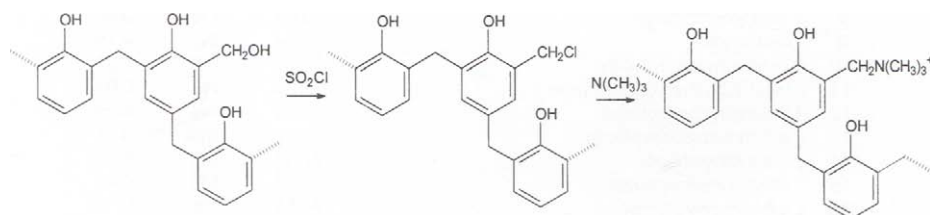
Peak	Compound	Ret. Time	MW	Area %
1	carbon dioxide	4.28	44	8.36
2	formaldehyde	4.93	30	4.25
3	methyl formate	6.67	60	0.15
4	methanol	10.60	32	2.65
5	water	18.49	18	3.23
6	benzofuran	49.11	118	0.23
7	2-methylbenzofuran	54.68	132	0.60
8	3-methylbenzofuran	55.60	132	0.34
9	1,2-ethandiol	56.14	62	0.15
10	4,7-dimethylbenzofuran	59.77	146	0.32
11	2-vinyl-2,3-dihydrobenzofuran	60.94	146	0.95
12	?,?-dimethylbenzofuran	61.10	146	trace
13	2,4,7-trimethylbenzofuran	65.84	160	0.51
14	2,3-dimethylphenol	72.00	122	9.77
15	2-ethyl-5-methylphenol	74.32	136	0.44
16	2,4,6-trimethylphenol	76.55	136	17.44

TABLE 8.3.1 (continued). Compounds identified in the pyrogram of a crosslinked phenol-formaldehyde resin sample shown in Figure 8.3.1.

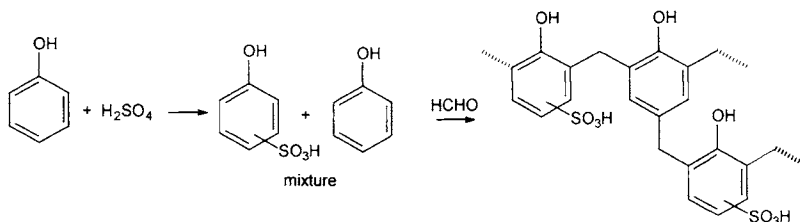
Peak	Compound	Ret. Time	MW	Area %
17	2-methylphenol	76.70	108	12.35
18	phenol	76.84	94	4.41
19	5-methyl-2(1-methylethyl)phenol	78.39	150	0.34
20	2-ethylphenol	79.99	122	0.48
21	2,4-dimethylphenol	80.53	122	18.08
22	4-methylphenol	81.04	108	9.60
23	3-ethyl-5-methylphenol	83.19	136	0.63
24	4-ethyl-3-methylphenol	84.51	136	0.58
25	4-ethylphenol	85.07	122	0.44
26	2-allyl-4-methylphenol ?	89.51	148	0.20
27	9H-xanthene	97.58	182	0.19
28	2-hydroxy-benz[a]naphthalene	102.23	194	1.22
29	6-benzyl-2-vinylphenol	104.52	210	0.88
30	?-benzyl-?-methyl-?-vinylphenol ?	109.39	224	0.48
31	6-benzyl-4-methyl-2-vinylphenol ?	110.47	224	0.53
32	6-benzyl-?-ethyl-?-vinylphenol ?	116.00	238	0.19

As seen from Figure 8.3.1 and Table 8.3.1, pyrolysis of the phenol-formaldehyde resin generates some formaldehyde probably eliminated from the methylol groups still present in the polymer, and also phenol and various alkyl substituted phenols that result from the breaking of the macromolecule network. Various studies (see e.g. [9]) showed that the decomposition mechanism of the polymer is initiated by bond rupture, which yields free radicals. The stabilization of the free radicals takes place by extraction of hydrogen atoms from the resin structure, leading to a decrease in the hydrogen/carbon ratio. The expected dimers of the methyl-substituted phenols, such as methyl-substituted dihydroxy-diphenylmethanes, which were expected to be formed, are thermally unstable and decompose to methyl-substituted phenols, or through cyclization to form methyl-substituted xanthenes. The cyclization occurs through water removal and not by hydrogen extraction.

Some phenol-formaldehyde resins have specific groups attached on the benzene rings with the purpose of generating ion exchange materials. For example, the inert resin can be modified by direct sulfonation into a strong cation exchanger. An anion exchanger also can be obtained after the polymerization process. The polycondensation in the presence of acid catalysts leaves a significant number of free $-\text{CH}_2\text{OH}$ groups. These can be further derivatized with SO_2Cl , and the $-\text{CH}_2\text{OH}$ groups are changed into $-\text{CH}_2\text{Cl}$ groups. Upon treatment with $(\text{CH}_3)_3\text{N}$, the resin can be changed into a strong anion exchange material by the following reactions:



The derivatization of the already polycondensed resin is not the only possibility to generate either cationic or anionic resins. One common procedure starts with the derivatization of the phenol prior to condensation. Sulfonic resins, for example, can be obtained following the reactions schematically shown below:



The sulfonation products of phenol can be condensed without separation, and a highly cross-linked material can be obtained in appropriate conditions. Other resins can be prepared similarly to sulfonic resins. For example starting with salicylic acid and formaldehyde, a resin with carboxylic groups is obtained.

The fixed ionic group also can be generated on the side chain of the resin. For example, condensation of sodium phenolate with Na_2SO_3 and HCHO leads to the formation of a resin with methylenesulfonic acid groups. Also, phenols such as resorcinol, naphthol, phenoxyacetic acid, and other aldehydes are used in the condensation instead of simple phenol and formaldehyde. For example, the condensation of phenoxyacetic acid and formaldehyde leads to a weak acid resin. Other variations of the condensation reaction are utilized, such as condensation of a phenol, a substituted benzaldehyde, and formaldehyde. Pyrolysis studies on ion exchange resins are common in literature [21–25]. Depending on the nature of the attached group, as well as on the proportion of the polymer that is derivatized, pyrolysis products originating from these groups can be seen in pyrolysates.

Another example for the flash pyrolysis results on a sample of a phenol formaldehyde type polymer is given in Figure 8.3.2 for poly[(phenyl glycidyl ether)-co-formaldehyde]. This is in fact a co-polymer since free phenol groups are still present in the material that was used as a sample (CAS# 28064-14-4 and $M_n = 345$). The pyrolysis was done similarly to that for other polymers exemplified in this book, at 600°C in He at a heating rate of 20°C/ms with 10 s THT. The separation was done on a Carbowax column (60 m, 0.32 mm i.d., 0.32 μm film thickness) with the GC starting at 40°C with a ramp of 2°C/min. up to 240°C and a final oven time of 20 min. (see Table 4.2.2). The MS was operated in EI+ mode. The peak identification for the chromatogram shown in Figure 8.3.2 was done using MS spectral library searches and is given in Table 8.3.2.

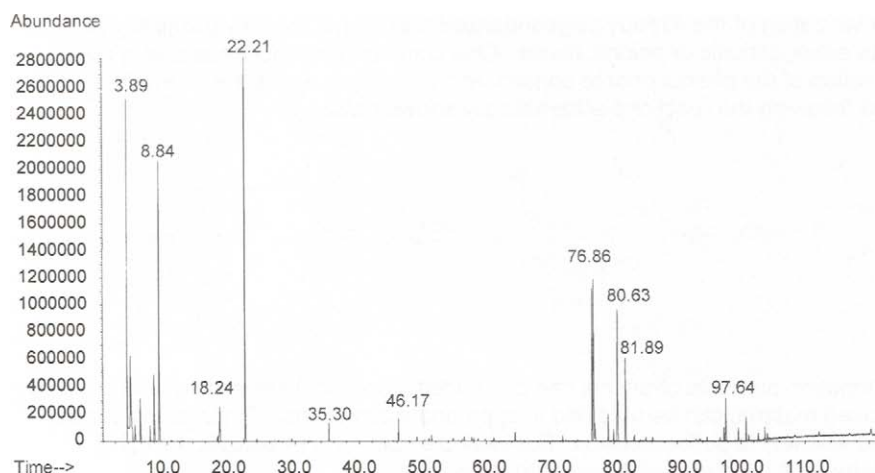


FIGURE 8.3.2. Pyrogram of a poly[(phenyl glycidyl ether)-co-formaldehyde] sample with $M_n = 345$. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 8.3.2. Compounds identified in the pyrogram of poly[(phenyl glycidyl ether)-co-formaldehyde] shown in Figure 8.3.2.

Peak	Compound	Ret. Time	MW	Area
1	carbon dioxide	4.40	44	11.62
2	propene	4.50	42	trace
3	methyloxirane	5.10	58	1.10
4	acetaldehyde	5.92	44	2.65
5	methoxyethene		58	trace
6	propanal	7.47	58	0.63
7	2-propanone (acetone)	8.12	58	4.44
8	2-propenal	8.94	56	15.86
9	ethanol	12.46	46	trace
10	toluene	17.95	92	trace
11	water	18.54	18	3.29
12	cyclobutenylmethanol	21.96	84	trace
13	2-propen-1-ol	22.49	58	20.72
14	1,3-dimethylbenzene	24.62	106	trace
15	2-methylfuran	29.45	82	trace
16	styrene	32.33	104	trace
17	1-hydroxy-2-propanone	35.30	74	0.90
18	acetic acid	45.25	60	trace
19	oxiranemethanol	46.17	74	1.01
20	benzofuran	49.15	118	trace
21	2,4,6-octatrienal	51.38	122	trace
22	3-methylbenzofuran	54.97	132	trace
23	2-methylbenzaldehyde	56.50	120	trace
24	4,7-dimethylbenzofuran	59.98	146	trace
25	2-vinyl-2,3-dihydrobenzofuran	61.25	146	trace
26	2-methylbenzofuran	64.51	132	trace

TABLE 8.3.2 (continued). Compounds identified in the pyrogram of poly[(phenyl glycidyl ether)-co-formaldehyde] shown in Figure 8.3.2.

Peak	Compound	Ret. Time	MW	Area
27	2-ethyl-5-methylphenol	74.63	136	trace
28	2-methylphenol	76.67	108	8.50
29	phenol	76.86	94	9.95
30	(phenoxy)methyl oxirane	77.05	150	1.00
31	[(2-methylphenoxy)methyl]oxirane	79.16	164	1.21
32	2-ethylphenol	79.97	122	trace
33	2,5-dimethylphenol	80.44	122	trace
34	4-methylphenol	80.63	108	8.75
35	[(4-methylphenoxy)methyl]oxirane	81.89	164	4.33
36	9H-xanthene	97.64	182	2.61
37	2-(2-methylpropyl)phenol	100.82	150	1.42

Some of the peaks in the pyrogram may result from the units of the polymer that have free phenol groups, and others may result from the ether group cleavage. Some compounds such as phenol, methylphenols, and dimethylphenols may come from both sources.

A similar polymer that allows further crosslinking by the opening of the oxirane ring is poly[(*o*-cresyl glycidyl ether)-co-formaldehyde], CAS# 29690-82-2. The pyrolysis of a sample with $M_n = 1,080$ of this material that also contains some free phenol groups is given in Figure 8.3.3. The pyrolysis was done in similar conditions with other polymers previously exemplified (see Table 4.2.2). The peak identification is given in Table 8.3.3.

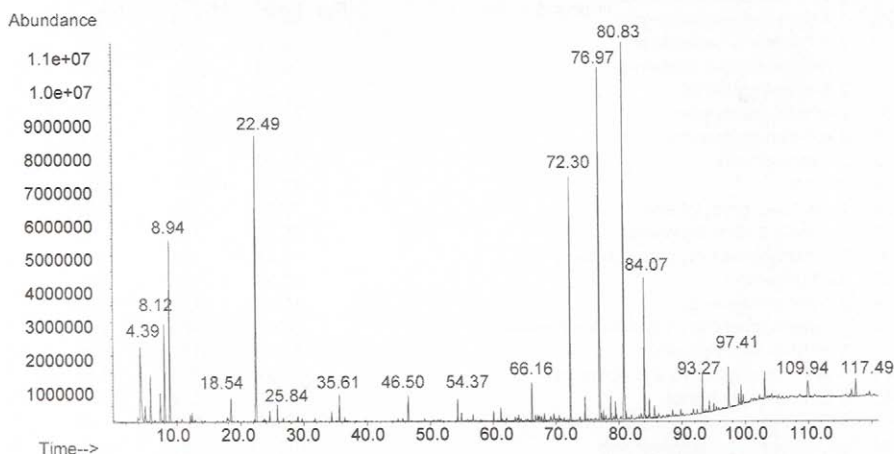


FIGURE 8.3.3. Pyrogram of a poly[(*o*-cresyl glycidyl ether)-co-formaldehyde] sample with $M_n = 1,080$. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 8.3.3. Compounds identified in the pyrogram of poly[(*o*-cresyl glycidyl ether)-co-formaldehyde] shown in Figure 8.3.3.

Peak	Compound	Ret. Time	MW	Area %
1	carbon dioxide	4.39	44	3.79
2	propene	4.50	42	0.89
3	methyloxirane	5.10	58	0.89
4	acetaldehyde	5.94	44	2.00
5	methoxyethene	6.56	58	
6	propanal	7.47	58	1.01
7	2-propanone (acetone)	8.12	58	4.28
8	2-propenal	8.94	56	6.50
9	methanol	10.75	32	trace
10	2-propanol	12.17	60	0.29
11	ethanol	12.46	46	0.36
12	toluene	17.95	92	trace
13	water	18.54	18	1.24
14	2-propen-1-ol	22.49	58	12.94
15	1,3-dimethylbenzene	24.62	106	0.66
16	1-(1-methylethoxy)-2-propanone	25.84	116	0.61
17	1,2,3-trimethylbenzene	34.38	120	0.36
18	1-hydroxy-2-propanone	35.61	74	0.98
19	oxiranemethanol	46.50	74	0.95
20	2,4-dimethylanisole	49.10	136	trace
21	1,2-propandiol	54.37	76	0.79
22	3-methylbenzofuran	54.97	132	0.39
23	2-methylbenzaldehyde	56.78	120	trace
24	4,7-dimethylbenzofuran	60.08	146	0.37
25	2-vinyl-2,3-dihydrobenzofuran	61.25	146	0.61
26	3,4-dimethylbenzaldehyde	64.03	134	trace
27	2,4,7-trimethylbenzofuran	66.17	160	1.44
28	p-isopropenylbenzaldehyde	68.16	146	0.45
29	2,6-dimethylphenol	72.30	122	8.94
30	2-ethyl-5-methylphenol	74.63	136	0.84
31	2,4,6-trimethylphenol	76.54	136	16.13
32	2-methylphenol	76.97	108	trace
33	phenol	77.20	94	trace
34	2-methyl-6-propylphenol	77.55	150	0.32
35	2-ethyl-4,5-dimethylphenol	78.70	150	0.80
36	[(2-methylphenoxy)methyl]oxirane	79.45	164	0.86
37	diethylphenol	80.55	150	trace
38	2,5-dimethylphenol	80.83	122	15.59
39	[(2-methylphenoxy)-1,2-dimethyl]oxirane	84.07	178	5.13
40	1-ethyl-3-methylphenol	84.82	136	0.96
41	1-(4-methoxyphenyl)-2-propanone	93.27	164	1.58
42	4-(2-propenyl)phenol	94.33	134	0.60
43	5-(2,2-dimethylethyl)-1,3-benzodioxole ?	97.41	178	1.97
44	α,α -dimethyl-benzeneethanol	103.12	150	1.09
45	2-[(3-benzylphenyl)methyl]oxirane	109.80	224	trace
46	isomer of 5-(2,2-dimethylethyl)-1,3-benzodioxole ?	109.94	178	1.53
47	2-[(3-benzylphenyl)-?]-dimethyl]oxirane	116.81	238	0.70
48	unknown [121(100), 64(22), 91(9), 77(5), 59(5)]	117.49		1.16

The identification of some of the peaks in the pyrograms of poly[(*o*-cresyl glycidyl ether)-co-formaldehyde] was done only tentatively. For example, the mass spectrum of [(2-

(methylphenoxy)methyl]oxirane is available in commercial mass spectral libraries and is shown in Figure 8.3.4.

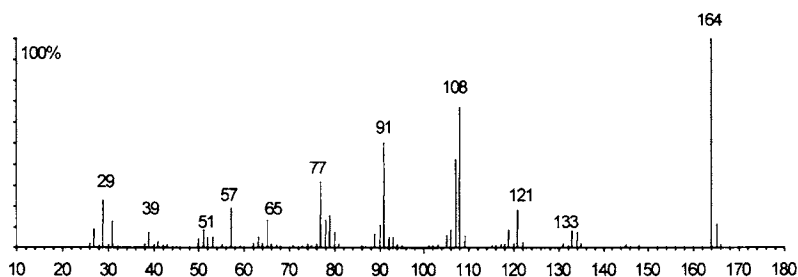


FIGURE 8.3.4. Spectrum of [(2-(methylphenoxy)methyl)oxirane available in NIST'98 mass spectral library.

On the other hand, the spectrum of [(2-(methylphenoxy)-1,2-dimethyl]oxirane is not available in common mass spectral libraries. The mass spectrum of the peak eluting at 84.07 min. in the pyrogram shown in Figure 8.3.3 is given in Figure 8.3.5 and was assigned to this compound by comparison with its next lower homolog.

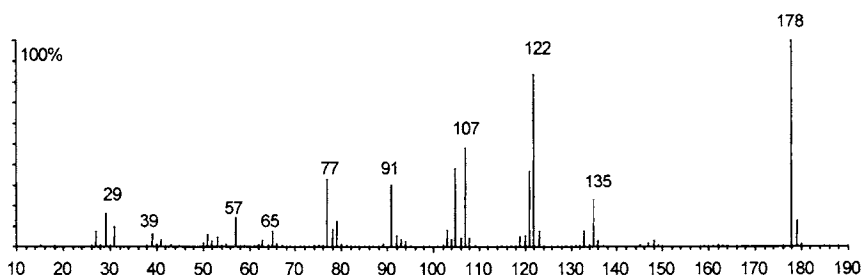


FIGURE 8.3.5. Spectrum assigned to [(2-(methylphenoxy)-1,2-dimethyl]oxirane.

As seen from Tables 8.3.2 and 8.3.3, the pyrolysis products of poly[(phenol glycidyl ether)-co-formaldehyde] and of poly[(*o*-cresyl glycidyl ether)-co-formaldehyde] give similar compounds. Some of these compounds are the result of the breaking of the polymeric network, some are the result of the elimination of the side groups to the benzene rings, and most compounds result from both processes, attached groups elimination and polymeric network cleavage.

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CHAPTER 9

*Polymers Containing Ether Groups in the Backbone***9.1 POLY(ETHERS)****- General aspects**

Polyethers are polymers containing ether groups in their backbone. The most common example of a polymer from this class is probably polyethylene glycol $H(OCH_2CH_2)_nOH$ (or PEG), also known as poly(ethylene oxide) (or PEO), with unspecified end groups and with the idealized formula $(-CH_2CH_2O-)_n$. Many other polyethers are used in practice including polypropylene oxide, poly(oxy-1,4-phenylene), poly(oxy-1,3-phenylene), or more complicated ethers that contain besides the ether group, other groups such as ketone. Two common polymers of this latter type are poly(oxy-1,4-phenylene-carbonyl-1,4-phenylene) or poly(ether ketone) (or PEK), and poly(oxy-1,4-phenylene-oxy-1,4-phenylene-carbonyl-1,4-phenylene) or poly(ether ether ketone) (or PEEK).

There are various procedures for the preparation of polyethers. These procedures typically start with oxirane or oxirane derivatives (e.g. propylene oxide, etc.). Base catalyzed anionic polymerization, acid initiation, or complex coordination catalysis can be used for the reaction [1–3]. Not only oxiranes can generate polyethers. Diols also can be used for polyether synthesis. Other source compounds include tetrahydrofuran, which can be polymerized to a polyether using fluorosulfonic acid (HSO_3F) as a catalyst, oxetane (trimethylene oxide) or oxetane derivatives, which can be polymerized to generate polyethers with practical applications such as poly[bis(chloromethyl)oxetane], etc.

An important group of polymers from this class are the epoxy resins. These polymers containing epoxy groups in a pre-polymer are used for crosslinking of other polymers or to form resin type materials containing ether groups in the backbone and hydroxyl side groups that impart strong adhesive properties. Poly(ethers) also are frequently used in copolymers.

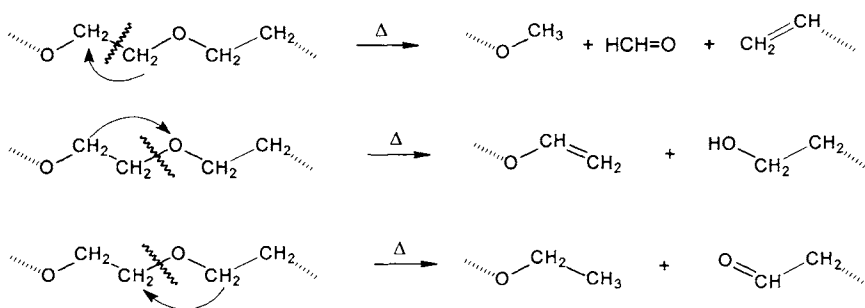
- Poly(ethylene glycol)

Poly(ethylene glycol) (PEG) or poly(ethylene oxide) (PEO) or poly(oxyethylene), CAS# 25322-68-3, can be made with various degrees of polymerization (various names are used interchangeably). The polymer with $M_w = 200$ –600 is a clear, colorless, viscous liquid. The polymer with $M_w = 600$ –3000 forms low melting waxy solids. The polymer with $M_w = 100,000$ –1,000,000 is a highly crystalline thermoplastic solid with physical properties similar to that of polyethylene but water soluble. PEO can have a linear or a branched molecule. Low M_w PEO is used for various purposes such as in making surfactants and thickeners, in various pharmaceutical applications, and in cosmetics (creams and lotions). Medium M_w polymers are used as adhesives, binders, plasticizers, lubricants, molding compounds, etc. High M_w PEO is used in textile sizing, hydrodynamic friction reducing agents, as a coating for seeds, and also in cosmetics,

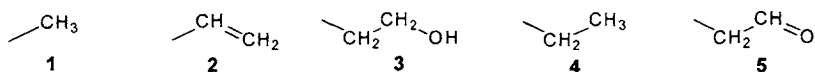
packaging, adhesives, and in materials for dentistry. The polymer can form complexes with electrolytes such as lithium chloride that have potential uses in batteries.

Several reports are available in literature regarding thermal decomposition of poly(ethylene oxide) not in flash pyrolysis conditions. One such report indicates that at temperatures between 324° C and 363° C, the polymer generates 9.7% of volatile compounds (at 25° C), 3.9% monomer with smaller amounts of CO₂, formaldehyde, ethanol, and saturated C₁-C₇ compounds [4]. Another report indicates that at temperatures between 225° C and 250° C, the polymer generates CO₂, HCHO, CH₃CHO and (CH₃CH₂)₂O. Other reports on PEG are also available in literature. These reports cover various conditions of decomposition, such as low-temperature pyrolysis [5], or thermooxidative degradation of the homopolymer with or without added salts. In thermooxidative degradation PEG forms similar products as in an inert atmosphere [6, 7]. At 280° C the decomposition products are reported to be diethyl ether, ethyl methyl ether, acetaldehyde, formaldehyde, CO₂, CO, ethene, cyclohex-3-ene-1'-one [6].

Flash pyrolysis studies on PEO showed that the degradation starts in the range 235–255° C with C-O and C-C bond scission, leading to a complex mixture of compounds. The possible bond cleavages are the following:





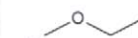







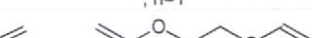





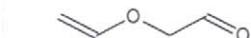


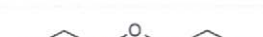

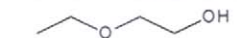



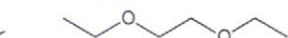

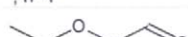




Five different groups can be distinguished at the end of the fragments formed in these reactions, each connected to an oxygen atom. These groups are the following:



Any combination of two such groups can form the ends of a molecule in the pyrolysate, leading to 15 possible combinations, which are listed in Table 9.1.1. The molecular mass of the molecule can be easily obtained using the expression $MW(a) + MW(b) + 16(O) + n \cdot 44(CH_2-CH_2-O)$, where "a" indicates the first end group, "b" the second end group, 16 is the atomic weight for oxygen, and 44 is the MW for the fragment -CH₂-CH₂-O-, which is the repeating unit in these molecules. The number of repetitions is indicated by "n", which can take both positive and in some cases negative integer values.

TABLE 9.1.1. Possible fragment molecules generated from the cleavage of PEO backbone.

Combination	Type	MW*	Examples
1,1	A	46+n-44	$n=0$  , $n=1$ 
1,2	B	58+n-44	$n=0$  , $n=1$ 
1,3	C	76+n-44	$n=0$  , $n=1$ 
1,4	D	60+n-44	$n=0$  , $n=1$ 
1,5	E	74+n-44	$n=-1$  , $n=0$  , $n=1$ 
2,2	F	70+n-44	$n=0$  , $n=1$ 
2,3	G	88+n-44	$n=-1$  , $n=0$ 
2,4	H	72+n-44	$n=-1$  , $n=0$  , $n=1$ 
2,5	I	86+n-44	$n=1$ 
3,3	J	106+n-44	$n=-2$  , $n=-1$  , $n=0$ 
3,4	K	90+n-44	$n=-1$  , $n=0$ 
3,5	L	104+n-44	$n=-1$  , $n=0$ 
4,4	M	74+n-44	$n=0$  , $n=1$ 
4,5	N	88+n-44	$n=-1$  , $n=1$ 
5,5	O	102+n-44	$n=-1$  , $n=0$ 

*Note: n can take negative or positive integer values.

Results for a Py-GC/MS analysis of a poly(ethylene glycol) sample, CAS# 25322-68-3, with $M_n = 1,000$ are shown in Figure 9.1.1. The pyrolysis was done in similar conditions as for other examples, at 600° C in He at a heating rate of 20° C/ms. with 10 s THT. The separation was done on a Carbowax column with the GC starting at 40° C with a ramp of 2° C/min. up to 240° C and a final oven time of 20 min. (see Table 4.2.2).

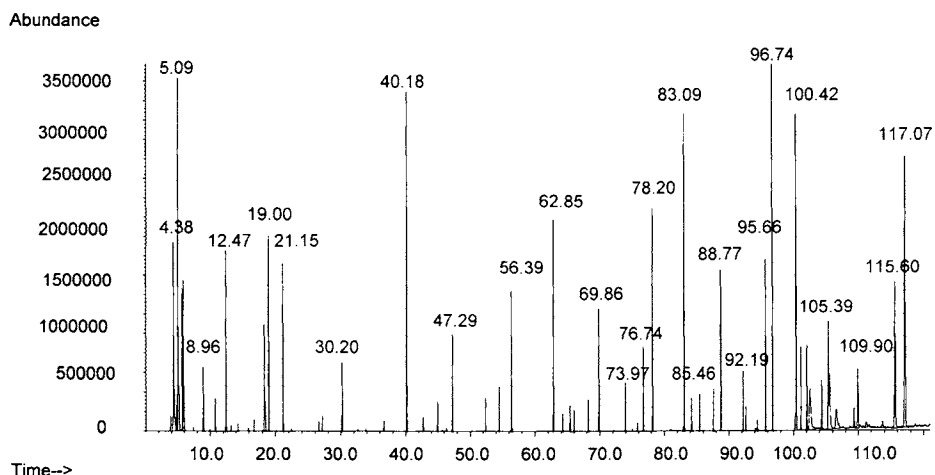


FIGURE 9.1.1. Result for a Py-GC/MS analysis of poly(ethylene glycol) $M_n = 1,000$. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

A different sample of PEG, having $M_n = 10,000$, was pyrolyzed in the same conditions as those used for the pyrolysis of the PEG sample with $M_n = 1,000$. The results for this sample are shown in Figure 9.1.2.

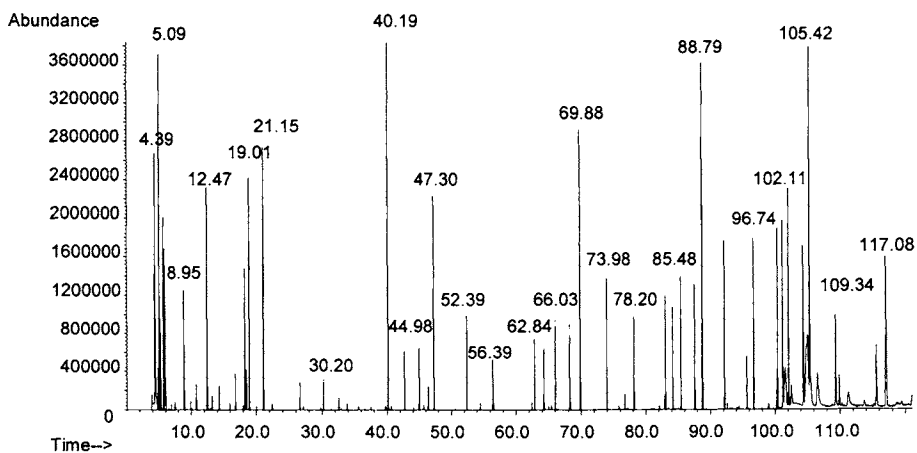


FIGURE 9.1.2. Result for a Py-GC/MS analysis of poly(ethylene glycol) $M_n = 10,000$. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

The peak identification for the chromatograms shown in Figures 9.1.1 and 9.1.2 was done using MS spectral library searches only and is given in Table 9.1.2. The retention

times of the two pyrograms are very close to each other, and only the retention times for the pyrogram from Figure 9.1.1 are shown in the table. In addition to the compound name, Table 9.1.2 also contains a column that indicates which compound type corresponds to those shown in Table 9.1.1. Except for the unsaturated aldehydes and dicarbonyl compounds (I and O types in Table 9.1.1), all the other types of compounds expected in the pyrolysate were identified. Area % in both chromatograms shown in Figure 9.1.1 and Figure 9.1.2 are given in the table, for comparison.

TABLE 9.1.2. Compounds identified in the pyrogram of poly(ethylene glycol) $M_n = 1,000$ and $M_n = 10,000$ as shown in Figure 9.1.1 and Figure 9.1.2, respectively.

Peak	Type*	Compound	Ret. Time	MW	Area % $M_n=1,000$	Area % $M_n=10,000$
1	H(-1)	ethene	4.38	28		
2	A0	dimethyl ether	4.63	46	trace	trace
3	D0	methoxyethane	4.88	60	trace	0.36
4	E(-1)	formaldehyde	5.09	30	5.63	5.45
5	B0	methoxyethene	5.12	58	trace	trace
6	M0	diethyl ether	5.18	74	trace	0.92
7	H0	ethyl vinyl ether	5.73	72	1.68	2.32
8	N(-1)	acetaldehyde	5.94	44	2.26	2.39
9		propanal	7.47	58	trace	trace
10		propenal (acrolein)	8.96	56	0.83	1.60
11	L(-1)	hydroxyacetaldehyde	10.81	60	0.46	0.32
12	A1	1,2-dimethoxyethane	11.97	90	trace	trace
13	K(-1)	ethanol	12.47	46	2.51	3.00
14		2-methyl-1,3-dioxolane	13.25	88	0.34	trace
15	D1	2-ethoxy-1-methoxyethane	14.33	104	trace	0.24
16	E0	methoxyacetaldehyde	15.97	74	0.29	trace
17	M1	1,2-diethoxyethane	16.82	118	0.33	0.40
18	B1	(2-methoxyethoxy)ethene	18.35	102	2.22	1.76
19	J(-2)	water	18.52	18	trace	0.77
20	L0	2-(2-hydroxyethoxy)ethanol	19.00	104	2.68	3.23
21		1,4-dioxane	19.53	88	trace	trace
22		2-methyl-1,3,6-trioxacyclooctane	20.13	132	trace	trace
23	H1	1-(2-ethoxyethoxy)ethene	21.15	116	2.35	3.29
24	F1	1,1'-[1,2-ethandiylbis(oxy)]bisethene	26.61	114	0.38	0.30
25	C0	2-methoxyethanol	27.11	76	0.49	trace
26	K0	2-ethoxyethanol	30.20	90	1.22	0.35
27	A2	1,1'-oxybis(2-methoxy)ethane	37.55	134	trace	trace
28	G0	2-(ethenyloxy)ethanol	40.18	88	5.15	5.95
29	M2	1,1'-oxybis(2-ethoxy)ethane	42.72	162	0.60	0.63
30	B2	1-[2-(2-methoxyethoxy)ethoxy]ethene	44.97	146	0.78	0.72
31		furfural	46.41	96	trace	0.36
32	H2	1-[2-(2-ethoxyethoxy)ethoxy]ethene	47.29	160	1.64	2.59
33	F2	1,1'-[oxybis(2,1-ethandiyloxy)]bisethene	52.39	158	0.84	1.03
34	C1	2-(2-methoxyethoxy)ethanol	54.48	120	1.09	trace
35	K1	2-(2-ethoxyethoxy)ethanol	56.39	134	2.39	0.63
36	G1	2-[2-(ethenyloxy)ethoxy]ethanol	62.85	132	3.33	0.80
37	A3	2,5,8,11-tetraoxadodecane	64.25	178	0.72	0.69

* Note: the number associated with each "Type" indicates how many repeating units $-\text{CH}_2-\text{CH}_2-\text{O}-$ with MW = 44 are present in the molecule.

TABLE 9.1.2 (continued). Compounds identified in the pyrogram of poly(ethylene glycol) $M_n = 1,000$ and $M_n = 10,000$ as shown in Figure 9.1.1 and Figure 9.1.2, respectively.

Peak	Type	Compound	Ret. Time	MW	Area % $M_n=1,000$	Area % $M_n=10,000$
38		1,4-dioxan-2-ol	65.40	104	0.97	trace
39	M3	triethyleneglycol diethylether	66.02	206	0.75	1.02
40	B3	1-[2-(2-methoxyethoxy)ethoxy]ethoxyethene	68.24	190	1.16	1.13
41	H3	1-[2-(2-ethoxyethoxy)ethoxy]ethoxyethene	69.86	204	2.50	3.59
42	F3	F3	73.97	202	1.14	1.56
43	J0	2,2'-oxybisethanol	75.82	106	0.48	trace
44	C2	2-[2-(2-methoxyethoxy)ethoxy]ethanol	76.74	164	1.74	trace
45	K2	2-[2-(2-ethoxyethoxy)ethoxy]ethanol	78.20	178	3.61	1.03
46	G2	G2	83.09	176	5.05	1.33
47	A4	2,5,8,11,14-pentaoxapentadecane	84.21	222	0.91	1.21
48	M4	tetraethylene glycol diethylether	85.46	250	0.98	1.64
49	B4	B4	87.60	234	1.09	1.46
50	H4	H4	88.77	248	2.84	4.86
51	F4	F4	92.19	246	1.17	2.12
52	J1	2,2'-[1,2-ethandiylbis(oxy)]bis-ethanol	92.61	150	0.40	0.40
53	C3	C3	93.36	208	0.77	trace
54	B5	B5	95.66	278	2.10	0.60
55	H5	H5	96.74	292	5.01	2.36
56	K3	2-[2-(2-ethoxyethoxy)ethoxy]ethoxyethanol	96.74	222	trace	trace
57	G3	G3	100.42	220	4.67	2.26
58	A5	2,5,8,11,14,17-hexaoxahexadecane (pentaethyleneglycol dimethylether)	101.17	266	1.20	2.83
59	M5	pentaethylene glycol diethylether	102.09	294	1.21	3.36
60		1,4,7,10,13,16-hexaoxacyclooctadecane	102.54	264	1.90	0.64
61	C4	C4	104.39	252	0.76	2.88
62	K4	pentaethylene glycol monoethyl ether	105.08	266	trace	5.22
63	H6	H6	105.39	336	2.92	7.90
64	F5	F5	109.41	290	trace	trace
65	J3	pentaethylene glycol	109.90	238	1.10	0.68
66	B6	B6	115.60	322	3.32	1.65
67	F6	F6	117.07	334	6.32	4.13

Peak identification in the pyrogram shown in Figure 9.1.2 cannot be based solely on the mass spectra, since some of these spectra are very similar, and the library searches give results with high probability for compounds basically made from the same units but with considerably different MW. As an example, the spectra for the series B_n (see Table 9.1.1) are shown in Figure 9.1.3. The differentiation between the compounds from the same series (e.g. A1, A2, A3, etc.) was done including the retention times as an additional parameter. The first two compounds in each series may have a spectrum with some differences, and the similarity becomes more pronounced at higher terms of each series.

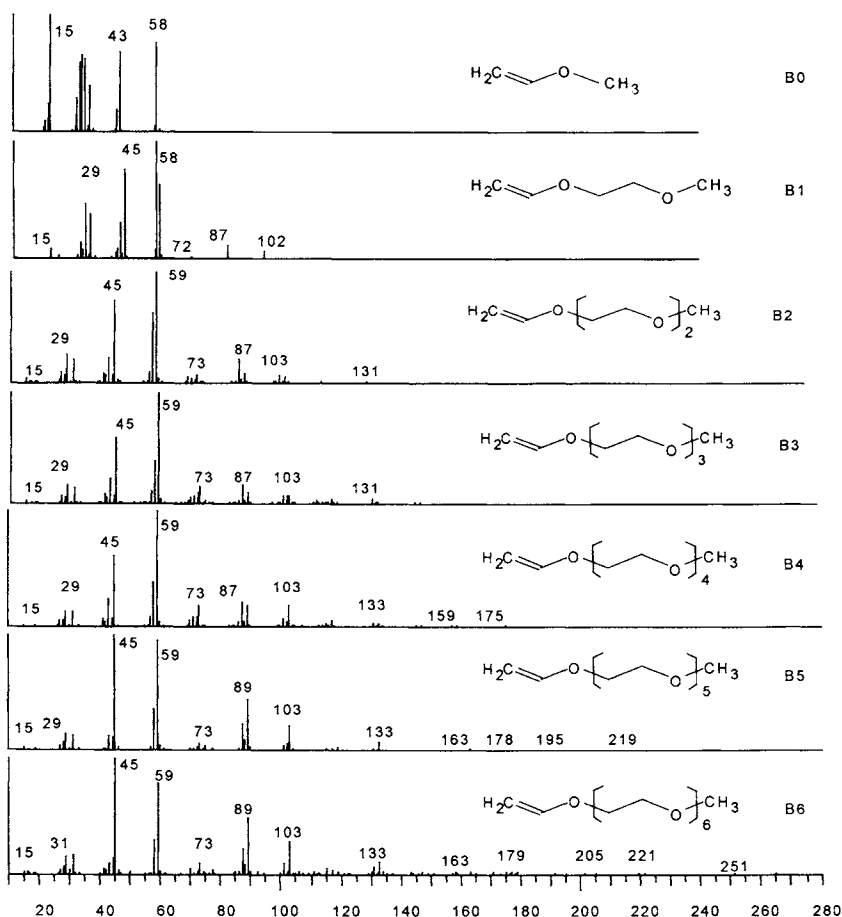


FIGURE 9.1.3. Mass spectra for the series B_n of compounds detected in the pyrolysis of PEG.

On the other hand, the differentiation between different series of compounds (indicated as A, B, C, etc.) was possible using the mass spectra in spite of the common repeating unit present in the compounds. These repeating units brought some similarity between the spectra, but identity was not achieved. The mass spectra for some of the compounds containing three $\text{CH}_2\text{-CH}_2\text{-O}$ units and different end groups (see Table 9.1.1) are shown in Figure 9.1.4. The spectra of the lower terms are available in common mass spectral libraries while some of the higher terms (with more than three $\text{CH}_2\text{-CH}_2\text{-O}$ units) are not available.

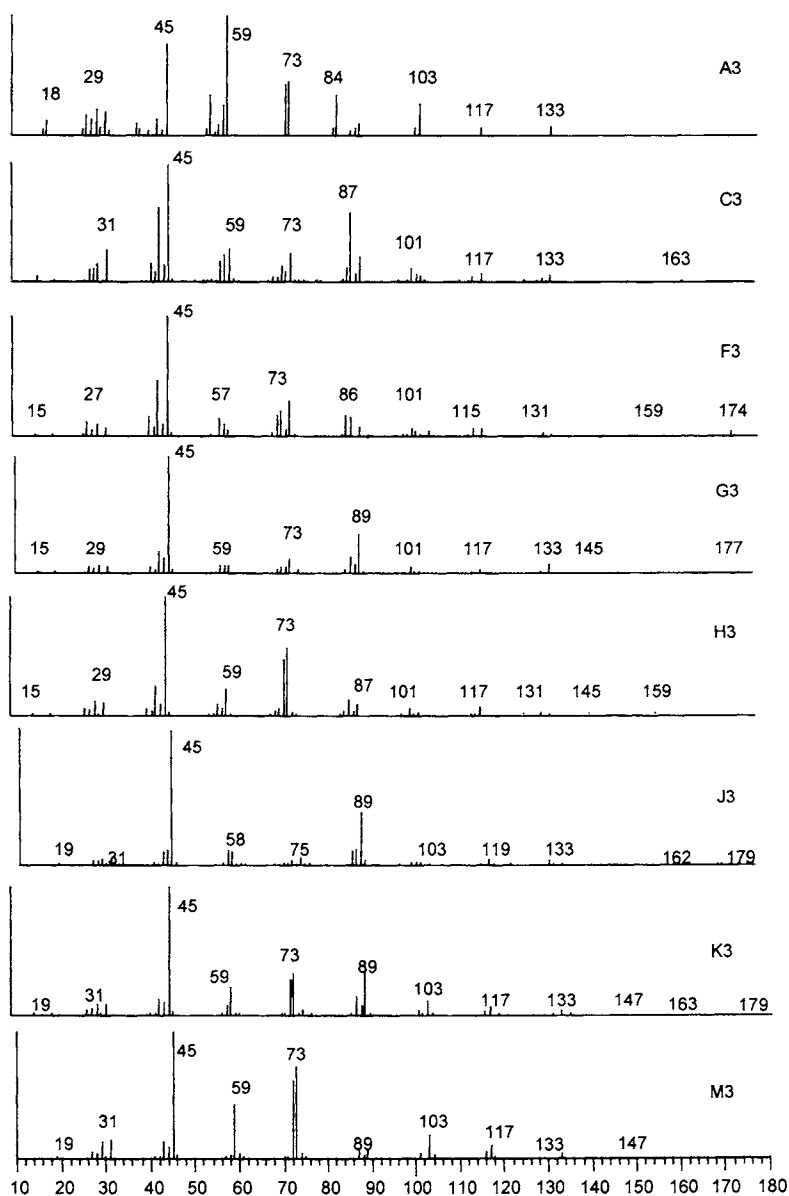


FIGURE 9.1.4. Mass spectra for compounds with three $\text{CH}_2\text{-CH}_2\text{-O}$ units and different end groups (types A3, C3, F3, etc.) detected in the pyrolysate of PEG.

The inspection of the variation of the area % values in Table 9.1.2 for the PEG samples with two different polymerization degrees shows that considerable variation can be seen from one polymer to the other. However, the nature of the compounds generated from the two polymers is the same.

One more example of pyrolysis results is given for poly(ethylene oxide) with $M_w = 300,000$ and is shown in Figure 9.1.5. The Py-GC/MS experiment was done in similar conditions as for other examples (see Table 4.2.2) and peak identification is given in Table 9.1.3.

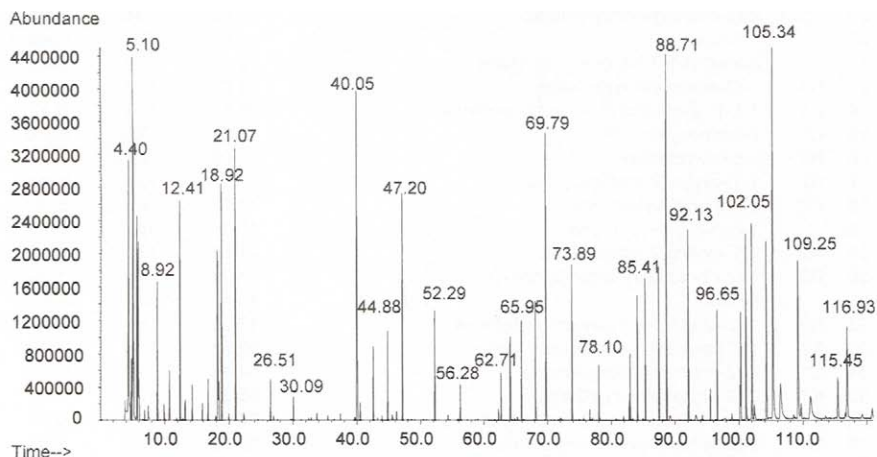


FIGURE 9.1.5. Result for a Py-GC/MS analysis of poly(ethylene oxide) $M_w = 300,000$. Pyrolysis done on 0.4 mg material at 600°C in He, with the separation on a Carbowax type column.

TABLE 9.1.3. Compounds identified in the pyrogram of poly(ethylene oxide) $M_w = 300,000$ as shown in Figure 9.1.5.

Peak*	Type	Compound	Ret. Time	MW	Area %
1	H(-1)	ethene	4.40	28	5.64
2	A0	dimethyl ether	4.63	46	trace
3	D0	methoxyethane	4.88	60	trace
4	E(-1)	formaldehyde	5.10	30	6.68
5	B0	methoxyethene	5.12	58	trace
6	M0	diethyl ether	5.18	74	trace
7	H0	ethyl vinyl ether	5.73	72	2.35
8	N(-1)	acetaldehyde	5.94	44	2.62
9		propanal	7.48	58	0.30
10		propenal (acrolein)	8.92	56	1.69
10a		butanal	9.93	72	0.16
11	L(-1)	hydroxyacetaldehyde	10.76	60	0.70
12	A1	1,2-dimethoxyethane	11.97	90	trace
13	K(-1)	ethanol	12.41	46	2.98
14		2-methyl-1,3-dioxolane	13.18	88	0.22
15	D1	2-ethoxy-1-methoxyethane	14.27	104	0.36
16	E0	methoxyacetaldehyde	15.88	74	0.16
17	M1	1,2-diethoxyethane	16.76	118	0.45
18	B1	(2-methoxyethoxy)ethene	18.27	102	2.82
19	J(-2)	water	18.52	18	trace

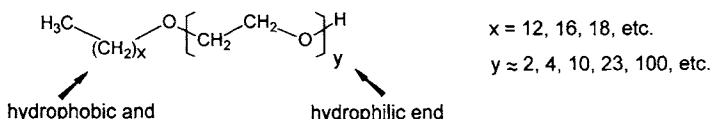
*Note: the peak numbers from Tables 9.1.2 and 9.1.3 are the same letter "a" showing new peaks.

TABLE 9.1.3 (continued). Compounds identified in the pyrogram of poly(ethylene oxide) $M_w = 300,000$ as shown in Figure 9.1.5.

Peak*	Type	Compound	Ret. Time	MW	Area %
20	L0	2-(2-hydroxyethoxy)ethanal	18.92	104	3.24
21		1,4-dioxane	19.53	88	trace
22		2-methyl-1,3,6-trioxacyclooctane	20.13	132	trace
23	H1	1-(2-ethoxyethoxy)ethene	21.07	116	3.39
24	F1	1,1'-[1,2-ethandiylbis(oxy)]bis-ethene	26.51	114	0.42
25	C0	2-methoxyethanol	27.11	76	trace
26	K0	2-ethoxyethanol	30.09	90	0.27
27	A2	1,1'-oxybis(2-methoxy)ethane	37.55	134	trace
28	G0	2-(ethenyloxy)ethanol	40.05	88	5.79
28a		1-hydroxy-2-butanone	40.56	88	0.23
29	M2	1,1'-oxybis(2-ethoxy)ethane	42.64	162	0.82
30	B2	1-[2-(2-methoxyethoxy)ethoxy]ethene	44.88	146	1.05
31		furfural	46.41	96	trace
32	H2	1-[2-(2-ethoxyethoxy)ethoxy]ethene	47.20	160	2.79
33	F2	1,1'-[oxybis(2,1-ethandiylloxy)]bisethene	52.29	158	1.26
34	C1	2-(2-methoxyethoxy)ethanol	54.48	120	trace
35	K1	2-(2-ethoxyethoxy)ethanol	56.28	134	0.44
35a	D2	1-(2-ethoxyethoxy)-2-methoxyethene	62.30	148	0.12
36	G1	2-[2-(ethenyloxy)ethoxy]ethanol	62.72	132	0.50
37	A3	2,5,8,11-tetraoxadodecane	64.17	178	0.96
38		1,4-dioxan-2-ol	65.40	104	trace
39	M3	triethyleneglycol diethylether	65.95	206	1.16
40	B3	1-[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]ethene	68.16	190	1.46
41	H3	1-[2-[2-ethoxyethoxy)ethoxy]ethoxy]-ethene	69.79	204	3.83
42	F3	F3	73.89	202	1.85
43	J0	2,2'-oxybisethanol	75.82	106	trace
44	C2	2-[2-(2-methoxyethoxy)ethoxy]ethanol	76.63	164	0.11
45	K2	2-[2-(2-ethoxyethoxy)ethoxy]ethanol	78.10	178	0.67
46	G2	G2	82.98	176	0.98
47	A4	2,5,8,11,14-pentaioxapentadecane	84.15	222	1.49
48	M4	tetraethylene glycol diethylether	85.41	250	1.75
49	B4	B4	87.54	234	1.89
50	H4	H4	88.71	248	5.03
51	F4	F4	92.13	246	2.29
52	J1	2,2'-[1,2-ethandiylbis(oxy)]bis-ethanol	92.61	150	0.20
53	C3	C3	93.36	208	trace
54	B5	B5	95.57	278	0.34
55	H5	H5	96.65	292	1.50
56	K3	2-[2-[2-(2-ethoxyethoxy)ethoxy]ethoxy]ethanol	96.74	222	trace
57	G3	G3	100.32	220	2.00
58	A5	2,5,8,11,14,17-hexaoxahexadecane (pentaethyleneglycol dimethylether)	101.13	266	2.74
59	M5	pentaethylene glycol diethylether	102.05	294	3.04
60		1,4,7,10,13,16-hexaoxacyclooctadecane	102.42	264	0.41
61	C4	C4	104.33	252	3.08
62	K4	pentaethylene glycol monoethyl ether	105.08	266	trace
63	H6	H6	105.35	336	7.91
64	F5	F5	109.26	290	3.51
65	J3	pentaethylene glycol	109.73	238	0.38
66	B6	B6	115.45	322	1.22
67	F6	F6	116.93	334	2.74

By comparing the pyrogram shown in Figure 9.1.5 with the one in Figure 9.1.2, the similarity is obvious. The retention times in the chromatogram from Figure 9.1.5 show some small differences compared to the one from Figure 9.1.2. Between the two experiments 73 different other samples were analyzed. Peak areas for the same compound in the two chromatograms show noticeable variability, as seen by comparing the values from Table 9.1.3 with those from Table 9.1.2.

Besides the use of PEG as is, poly(ethylene glycols) with specific end groups are also commercially available. The compounds having one ether end group connected to a long alkyl chain are used as nonionic surfactants. This structure leads to one hydrophilic group (polar group) at one end of the molecule and a hydrophobic group at the other end, as shown below:



Some of these compounds are known under the name Brij[®]. These compounds have different numbers of oxyethylene units and different alkyl end groups. One surfactant from this group is Brij[®] 35, CAS# 9002-92-0. The chemical name of this material is polyoxyethylene(23) lauryl ether and it has the idealized formula $\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_n\text{OH}$, with $n \approx 23$. The pyrogram of this material was generated in He at 600° C, using conditions similar to those for the other examples of pyrolyzed polymers discussed in this book (see Table 4.2.2). The pyrogram is shown in Figure 9.1.6 and the peak identification is given in Table 9.1.4.

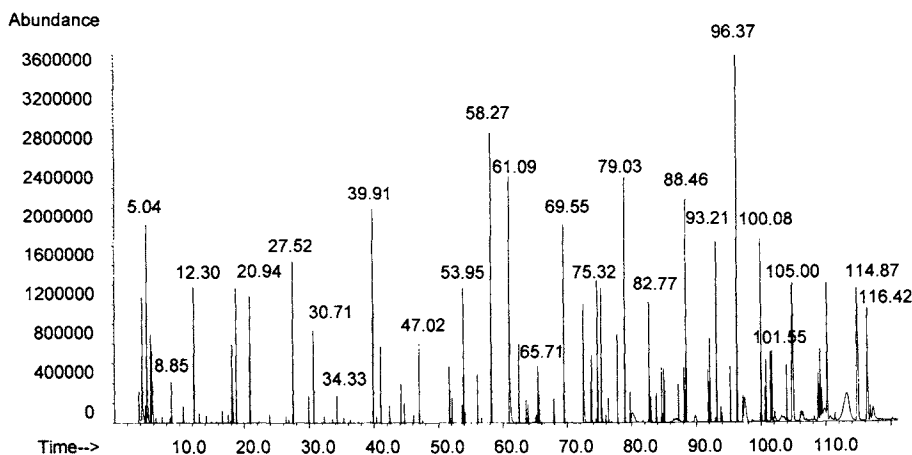


FIGURE 9.1.6. Result for a Py-GC/MS analysis of poly(oxyethylene)(23) lauryl ether (Brij[®] 35). Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 9.1.4. Compounds identified in the pyrogram of poly(oxyethylene)(23) lauryl ether (Brij® 35) as shown in Figure 9.1.6.

Peak	Type*	Compound	Ret. Time	MW	Area %
1	H(-1)	ethene	4.35	28	2.22
2	A0	dimethyl ether	4.63	46	trace
3	D0	methoxyethane	4.84	60	0.20
4	E(-1)	formaldehyde	5.04	30	3.26
5	B0	methoxyethene	5.12	58	trace
6	M0	diethyl ether	5.18	74	trace
7	H0	ethyl vinyl ether	5.67	72	1.07
8	N(-1)	acetaldehyde	5.88	44	1.12
9		propanal	7.48	58	trace
10		propenal (acrolein)	8.85	56	0.48
11		butanal	9.93	72	trace
12	L(-1)	hydroxyacetaldehyde	10.66	60	0.22
13	A1	1,2-dimethoxyethane	11.97	90	trace
14	K(-1)	ethanol	12.30	46	1.71
15		2-methyl-1,3-dioxolane	13.18	88	trace
16	D1	2-ethoxy-1-methoxyethane	14.27	104	trace
17	E0	methoxyacetaldehyde	15.88	74	trace
18	M1	1,2-diethoxyethane	16.62	118	0.12
19	B1	(2-methoxyethoxy)ethene	18.15	102	0.89
20	J(-2)	water	18.29	18	0.40
21	L0	2-(2-hydroxyethoxy)ethanal	18.80	104	1.68
22		1,4-dioxane	19.23	88	trace
23		2-methyl-1,3,6-trioxacyclooctane	19.58	132	trace
24	H1	1-(2-ethoxyethoxy)ethene	20.94	116	2.15
25	F1	1,1'-[1,2-ethandiylbis(oxy)]bisethene	26.38	114	trace
26	C0	2-methoxyethanol	26.95	76	trace
27		dodecane	27.52	170	2.08
28	K0	2-ethoxyethanol	29.93	90	0.30
29		1-dodecene	30.72	168	1.10
30		tridecane	34.33	184	0.30
31	A2	1,1'-oxybis(2-methoxy)ethane	37.35	134	trace
32	G0	2-(ethenyloxy)ethanol	39.91	88	3.04
33		1-hydroxy-2-butanone	40.36	88	trace
34		tetradecane	41.06	198	0.93
35	M2	1,1'-oxybis(2-ethoxy)ethane	42.44	162	0.22
36		1-tetradecene	44.22	196	0.44
37	B2	1-[2-(2-methoxyethoxy)ethoxy]ethene	44.70	146	0.20
38		furfural	46.21	96	trace
39	H2	1-[2-(2-ethoxyethoxy)ethoxy]ethene	47.02	160	0.80
40		methyl-?,?-decadienyl ether	51.73	168	0.67
41	F2	1,1'-[oxybis(2,1-ethandiylloxy)]bisethene	52.12	158	0.23
42		hexadecane	53.72	226	0.20
43		ethyl dodecyl ether	53.95	168	1.70
44	C1	2-(2-methoxyethoxy)ethanol	54.17	120	0.10
45	K1	2-(2-ethoxyethoxy)ethanol	56.08	134	0.55
46		vinyl lauryl ether	58.27	212	4.08
47		dodecanal	61.09	184	4.82
48	D2	1-(2-ethoxyethoxy)-2-methoxyethene	62.10	148	trace
49	G1	2-[2-(ethenyloxy)ethoxy]ethanol	62.54	132	0.88
50		methyl 6,8-dodecadienyl ether	63.64	196	0.27
51	A3	2,5,8,11-tetraoxadodecane	63.94	178	0.17
52		methyl ?,?-dodecadienyl ether	65.50	196	0.67

TABLE 9.1.4 (continued). Compounds identified in the pyrogram of poly(oxyethylene)(23) lauryl ether (Brij® 35) as shown in Figure 9.1.6.

Peak	Type*	Compound	Ret. Time	MW	Area %
53		1,4-dioxan-2-ol	65.71	104	0.26
54	M3	triethyleneglycol diethylether	65.75	206	trace
55	B3	1-[2-(2-(2-methoxyethoxy)ethoxy)ethoxy]ethene	67.94	190	0.36
56	H3	1-[2-(2-ethoxyethoxy)ethoxy]ethoxyethene	69.55	204	2.95
57		tetradecanal	72.56	212	2.26
58	F3	F3	73.68	202	0.38
59		(2-dodecyloxyethoxy)ethane in mix	73.84	258	0.82
60		dodecanol	74.75	186	1.92
61		2-(dodecyloxy)methoxyethane	75.32	244	1.71
62	J0	2,2'-oxybisethanol	75.62	106	trace
63	C2	2-[2-(2-methoxyethoxy)ethoxy]ethanol	76.41	164	0.24
64	K2	2-[2-(2-ethoxyethoxy)ethoxy]ethanol	77.87	178	0.99
65		1-(2-dodecyloxyethoxy)ethene	79.03	256	3.34
66		1-(ethenyloxy)hexadecane ?	79.80	268	0.35
67	G2	G2	82.77	176	1.43
68		hexadecanal ?	83.00	240	0.49
69		unknown [77(100), 57(78), 71(64), 85(45), 43(43),...227(3)]	83.79		0.30
70	A4	2,5,8,11,14-pentaoxapentadecane	83.89	222	0.31
71		tetradecanol ?	84.68	214	0.89
72		2-(2-dodecyloxyethoxy)ethanal	85.04	272	0.66
73	M4	tetraethylene glycol diethylether	85.14	250	0.45
74	B4	B4	87.29	234	0.38
75		2-(dodecyloxy)ethanol	88.17	230	0.70
76	H4	H4	88.47	248	3.05
77	F4	F4	91.88	246	0.59
78		unknown	92.16		1.04
79	J1	2,2'-[1,2-ethandiylbis(oxy)]bisethanol	92.31	150	trace
80		dodecyl ether	93.21		2.34
81	C3	C3	93.06	208	trace
82		dodecyl ether	93.81	242	0.21
83	B5	B5	95.32	278	0.64
84	H5	H5	96.37	292	5.92
85		dodecyl ether			trace
86	G3	G3	100.08	220	2.46
87		nonadecanal ?	100.67	282	0.44
88	A5	2,5,8,11,14,17-hexaoxahexadecane (pentaethyleneglycol dimethylether)	100.84	266	0.77
89		dodecyl ether	101.56		0.97
90	M5	pentaethylene glycol diethylether	101.74	294	0.97
91		1,4,7,10,13,16-hexaoxacyclooctadecane	102.13	264	0.33
92	C4	C4	104.01	252	0.84
93		dodecyl ether	104.84	266	2.60
94	H6	H6	105.00	336	2.56
95	F5	F5	108.87	290	0.90
96		dodecyl ether	109.15		1.40
97	J3	pentaethylene glycol	109.39	238	0.72
98		dodecyl ether	110.24		3.02
99	B6	B6	114.87	322	4.60
100	F6	F6	116.42	334	3.19

Peak identifications for the compounds in Brij[®] pyrolysate was based on mass spectral library searches and on comparison with the pyrolysis products of PEG. Some of the compounds are only tentatively identified, such as 1-(2-dodecyloxyethoxy)ethene with the spectrum given in Figure 9.1.7.

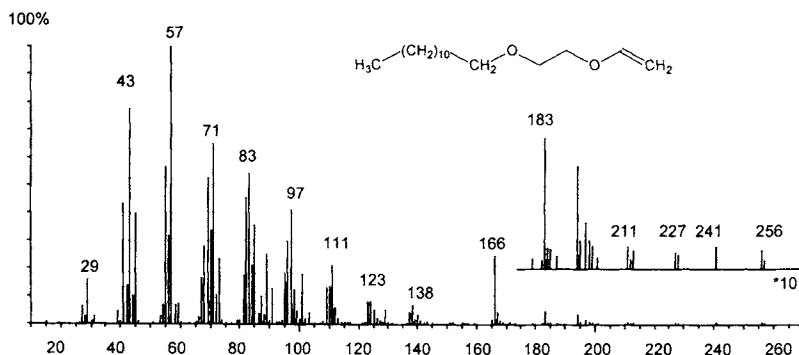
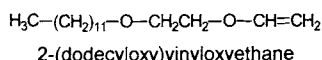
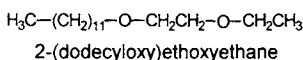
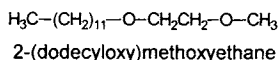
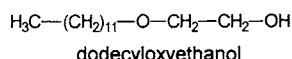
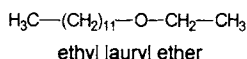
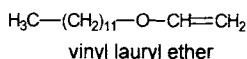
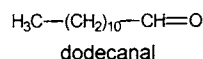
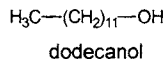
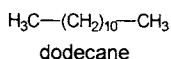
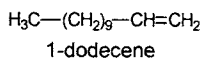


FIGURE 9.1.7. Mass spectrum tentatively identified as that of 1-(2-dodecyloxyethoxy)ethene.

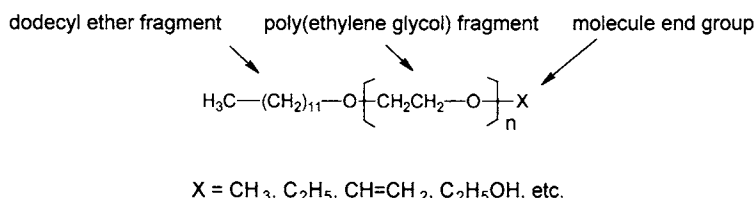
The composition of Brij[®] 35 pyrolysate is in many respects similar to that of PEG. A number of fragment molecules in the pyrolysate are generated from the PEG moiety and are identical to those obtained from PEG pyrolysis. The retention times for these compounds in the pyrogram shown in Figure 9.1.6 are slightly shifted (with up to 30 s) compared to those shown in Figure 9.1.5. Between the two pyrograms there were about 300 other samples analyzed, and the properties of the column were probably slightly modified.

The bonds C–C are more stable than the C–O bonds, and the molecular fragments generated from the cleavage of the polymer end contain the intact dodecyl group. Some of the compounds containing this group and identified in the pyrolysate are shown below:

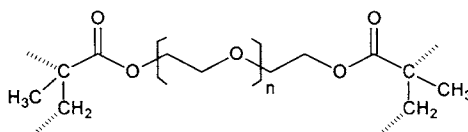


The detection of ether molecules containing both C₁₂ and C₂ units indicate a polyether with both units in the molecule, and not a mixture of PEG with a compound containing a long aliphatic chain.

In addition to the compounds that have a structure compatible with that of the polymer, some C_{16} molecules were tentatively identified in the pyrolysate of Brij[®]. These molecules were either incorrectly identified (by using mass spectral library search), or they are an impurity in the sample used for pyrolysis. Other dodecyl ethers were detected in the pyrolysate, but they were more difficult to identify unambiguously. The generic formula for these ethers is shown below:



PEG with other end groups, such as those allowing attachment of PEG fragments to other polymer backbones are also available. The PEG bridges between other polymer chains are used in specially designed polystyrenes, polyacrylates, and polybutadiene. In the copolymer formed in this way, PEG acts as a flexible crosslinker, which has many practical applications [8]. Poly(acrylic acid) or poly(methacrylic acid) with the carboxyl group esterified with di-, tri-, tetra-ethyleneglycol are used in laser video discs (these polymers can be considered as having a carbon chain backbone). Polymers where the ether chain is much longer (up to 1000 DP) and the end groups are acrylate or methacrylate also are known. They are used as crosslinking agents for other vinyl polymers forming macromolecules with the model structure shown below:



Pyrolysis of poly(ethylene glycol) with acrylate, methacrylate, or other end groups shows that, when the PEG segment is long enough, the pyrogram contains a significant number of peaks identical to those from the PEG pyrolysate. The end groups, alone or connected with fragments of ethylene glycol oligomer, also can be seen in the pyrolysate. As an example, the pyrogram from a sample of poly(ethylene glycol) dimethacrylate with the formula $H_2C=C(CH_3)CO(-OCH_2CH_2-)_nOOCCH(CH_3)=CH_2$, CAS# 25852-47-5, $M_n = 875$, is shown in Figure 9.1.8. Monomethyl ether hydroquinone has been used as an inhibitor in polymer synthesis. The experimental conditions for the Py-GC/MS experiment were the same as for other examples previously presented (see Table 4.2.2). Peak identification obtained by mass spectra library searches only is given in Table 9.1.5.

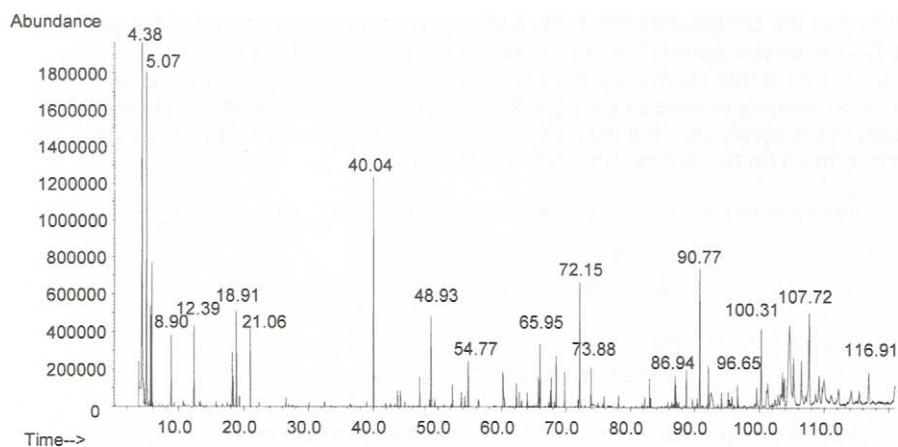


FIGURE 9.1.8. Result for a Py-GC/MS analysis of poly(ethylene glycol) dimethacrylate $M_n = 875$. Pyrolysis done on 0.4 mg material at 600°C in He, with the separation on a Carbowax type column.

TABLE 9.1.5. Compounds identified in the pyrogram of poly(ethylene glycol) dimethacrylate $M_n = 875$ as shown in Figure 9.1.8.

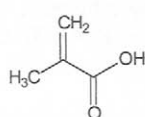
Peak*	Compound	Ret. Time	MW	Area %
1	ethene	4.38	28	14.60
2	formaldehyde	5.09	30	10.20
3	ethyl vinyl ether	5.73	72	2.39
4	acetaldehyde	5.91	44	4.10
5*	propenal (acrolein)	8.90	56	1.94
6	ethanol	12.40	46	2.17
7	(2-methoxyethoxy)ethene	18.27	102	1.61
8	water	18.36	18	1.23
9	2-(2-hydroxyethoxy)ethanal	18.91	104	2.71
10	2-(2-hydroxyethoxy)ethanol	21.06	116	1.83
11	1,1'-[1,2-ethandiylbis(oxy)]bisethene	26.50	114	trace
12	2-ethoxyethanol	30.10	90	trace
13	2-(ethenyloxy)ethanol	40.04	88	7.48
14	1-[2-(2-methoxyethoxy)ethoxy]ethene	44.70	146	trace
15*	1-[2-(2-ethoxyethoxy)ethoxy]ethene	47.20	160	0.55
16	2-methoxyethyl 2-methyl-2-propenoate	48.93	144	2.93
17*	1,1'-[oxybis(2,1-ethandiylloxy)]bisethene	52.29	158	0.50
18	dihydro-3-methyl-2(3H)-furanone	54.77	100	1.67
19*	2-(2-ethoxyethoxy)ethanol	56.30	134	trace
20*	2-methyl-2-propenoic acid	60.13	86	1.84
21	3-methyl-2(5H)-furanone	62.25	98	0.90
22*	2-oxepanone ?	65.69	114	1.10
23*	2-methyl-2-propenoic acid 2-hydroxyethyl ester	65.95	130	2.12
24*	2-ethoxyethyl methacrylate	67.71	158	0.88
25	2-methyl-2-propenoic acid 1,2-ethanediyl ester	68.45	198	1.69

* Note: peaks with * at the peak number contain a methacrylate moiety or are a result of the methacrylate moiety decomposition.

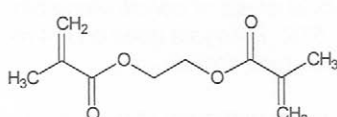
TABLE 9.1.5 (continued). Compounds identified in the pyrogram of poly(ethylene glycol) dimethacrylate $M_n = 875$ as shown in Figure 9.1.8.

Peak	Compound	Ret. Time	MW	Area %
26*	1-[2-[2-ethoxyethoxy]ethoxy]ethoxy]ethene	69.78	204	0.73
27	2-methyl-2-propenoic acid 2-(2-hydroxyethoxy)ethan-1-ol ester (diethyleneglycol dimethacrylate)	72.15	242	4.14
28	F3	73.88	202	1.04
29	2-[2-(2-ethoxyethoxy)ethoxy]ethanol	78.10	178	trace
30	diethyleneglycol monomethacrylate	81.99	174	trace
31	2-[2-(ethenyloxy)ethoxy]ethanol	82.98	132	0.59
32*	2,2'-oxybisethanol dipropionate	86.93	218	1.08
33	H4	88.69	248	0.92
34	triethyleneglycol dimethacrylate	90.77	286	4.91
35	F4	92.11	246	1.26
36	H5	96.65	292	0.55
37*	G3	100.31	220	3.48
38*	H6	105.31	336	3.54
39	tetraethyleneglycol monomethacrylate	106.51	260	2.19
40	tetraethyleneglycol dimethacrylate	107.72	330	6.71
41	F5	109.23	290	2.20
42	F6	116.91	334	2.17

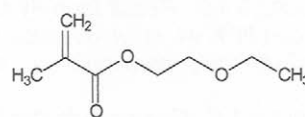
The structures of some of the molecules generated by pyrolysis of poly(ethylene glycol) dimethacrylate that retain the methacrylic acid (2-methyl-2-propenoic acid) moiety are shown below:



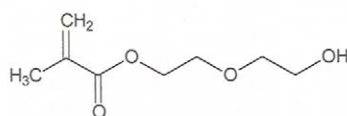
2-methyl-2-propenoic acid (MW = 86)



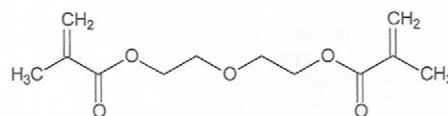
2-methyl-2-propenoic acid 1,2-ethanediyl ester (MW = 198)



2-ethoxyethyl methacrylate (MW = 158)



diethyleneglycol mono methacrylate (MW = 174)



dimethyleneglycol dimethacrylate (MW = 242)

The presence of di- tri- or tetra-ethylene glycol methacrylates in the pyrolysate may be caused by the presence of these compounds in the starting polymer.

- Copolymers of ethylene glycol

Poly(ethylene glycol) is used in a number of copolymers, such as poly(propylene oxide-co-ethylene oxide), polyethylene-*block*-poly(ethylene glycol), poly [2,2-propanebis(4-phenyl)carbonate-*block*-poly(ethylene oxide)], as well as in various polymer blends. Several pyrolysis studies were done on these copolymers [9–11].

An example of pyrolysis results for a copolymer of poly(ethylene glycol) is given below for poly(ethylene-*block*-poly(ethylene glycol) 20% wt. ethylene oxide, CAS# 97953-22-5 with $M_n = 575$. The pyrogram is shown in Figure 9.1.9. The idealized formula of the copolymer is $\text{CH}_3\text{CH}_2(\text{CH}_2\text{CH}_2)_x(\text{OCH}_2\text{CH}_2)_y\text{OH}$. The experimental conditions for the Py-GC/MS experiment were the same as for other examples previously presented (see Table 4.2.2). Peak identification obtained by mass spectra library searches only is given in Table 9.1.6.

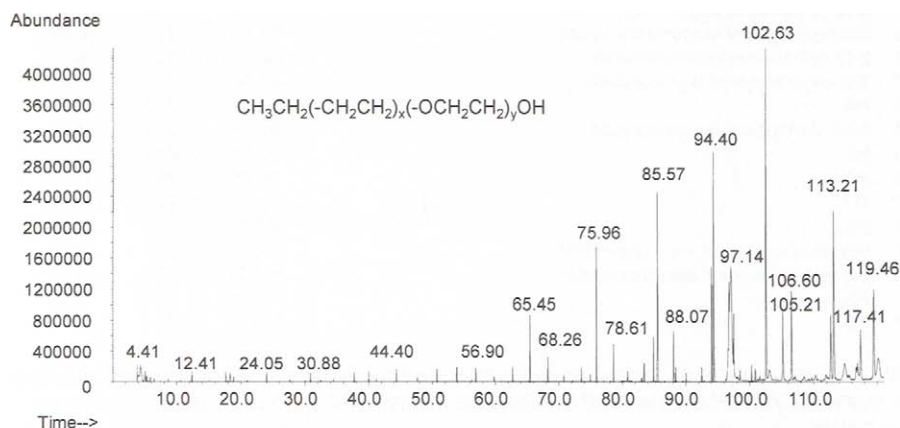


FIGURE 9.1.9. Result for a Py-GC/MS analysis of poly(ethylene-*block*-poly(ethylene glycol) 20% wt. ethylene oxide $M_n = 575$. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 9.1.6. Compounds identified in the pyrogram of poly(ethylene-*block*-poly(ethylene glycol) 20% wt. ethylene oxide $M_n = 575$ as shown in Figure 9.1.9.

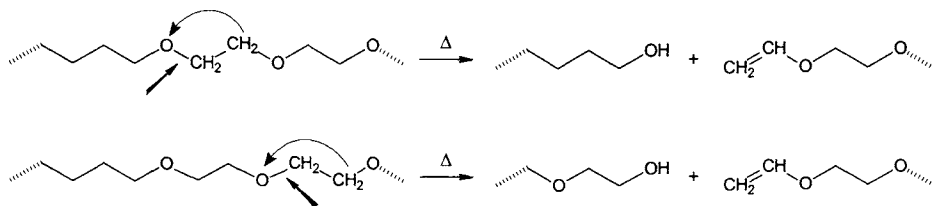
Peak	Compound	Ret. time	MW	Area %
1	ethene	4.41	28	1.48
2	ethane	5.11	30	0.46
3	1-hexene	5.38	84	trace
4	acetaldehyde	5.94	44	trace
5	1-heptene	6.67	98	trace
6	1-octene	8.85	112	trace
7	nonane	10.65	128	trace
8	ethanol	12.41	46	0.32
9	decane	15.21	142	trace
10	1-decene	17.69	140	0.29
11	(2-methoxyethoxy)ethene	18.27	102	trace
12	water	18.35	18	0.49
13	3-pentanol	18.78	88	trace
14	1-(2-ethoxyethoxy)ethene	21.07	116	trace
15	1-undecene	24.05	154	0.27
16	dodecane	27.75	170	trace
17	2-ethoxyethanol	30.09	90	trace
18	1-dodecene	30.88	168	0.24

TABLE 9.1.6 (continued). Compounds identified in the pyrogram of polyethylene-block-poly(ethylene glycol) 20% wt. ethylene oxide $M_n = 575$ as shown in Figure 9.1.9.

Peak	Compound	Ret. time	MW	Area %
19	tridecane	34.59	184	trace
20	1-tridecene	37.73	182	0.25
21	2-(ethenyloxy)ethanol	40.02	88	0.25
22	tetradecane	41.31	198	trace
23	1-tetradecene	44.40	196	0.34
24	1-[2-(2-ethoxyethoxy)ethoxy]ethene	47.18	160	trace
25	pentadecane	47.71	212	trace
26	1-pentadecene	50.80	210	0.35
27	hexadecane	53.91	226	0.39
28	2-(2-ethoxyethoxy)ethanol	56.26	134	trace
29	1-hexadecene	56.90	224	0.38
30	heptadecane	59.78	240	trace
31	1-heptadecene	62.72	238	0.40
32	octadecane	65.45	254	2.18
33	1-octadecene	68.26	252	0.75
34	1-[2-[2-ethoxyethoxy]ethoxy]ethoxy]ethene	69.76	204	trace
35	nonadecane	70.79	268	trace
36	1-nonadecene	73.55	266	0.42
37	1-dodecanol	74.96	186	trace
38	n-eicosane	75.96	282	4.59
39	2-[2-(2-ethoxyethoxy)ethoxy]ethanol	78.08	178	trace
40	eicos-1-ene	78.61	280	1.25
41	heneicosane	80.83	296	0.29
42	G2	82.96	176	trace
43	1-heneicosene	83.43	294	0.61
44	1-tetradecanol	84.91	214	1.45
45	n-docosane	85.57	310	6.92
46	1-docosene	88.07	308	1.73
47	2-(dodecyloxy)ethanol	88.42	230	0.45
48	n-tricosane	90.03	324	0.29
49	1-tricosene	92.50	322	0.48
50	1-hexadecanol	94.07	242	3.97
51	n-tetracosane	94.40	338	8.80
52	H5	96.66	292	1.87
53	1-tetracosene	96.78	336	5.21
54	2-(tetradecyloxy)ethanol	97.53	258	3.25
55	n-pentacosane	98.51	352	0.39
56	G3	100.31	220	0.50
57	1-pentacosene	100.87	350	0.47
58	n-hexacosane	102.63	366	15.07
59	1-hexacosene	105.21	364	3.73
60	2-(hexadecyloxy)ethanol	106.60	286	4.45
61	n-octacosane	112.75	394	4.07
62	1-octadecanol	113.21	270	10.33
63	hexadec-15-enyloxy-1-ethanol	117.41	284	3.67
64	2-(octadecyloxy)ethanol	119.46	314	6.90

The list of compounds identified in the pyrolysate of the copolymer shows the presence of polyethylene sequences, as well as of poly(ethylene glycol) sequences. However, a series of compounds such as 1-dodecanol, 1-tetradecanol, 1-hexadecanol, 2-(dodecyloxy)ethanol, 2-(tetradecyloxy)ethanol, 2-(hexadecyloxy)ethanol, hexadec-15-enyloxy-1-ethanol, and 2-(octadecyloxy)ethanol are also present in the pyrolysate,

accounting for a considerable proportion of the compounds seen by the GC/MS analysis. Since the polymer is indicated as *block* type, the presence of these compounds that are of AB type (A = ethene, B = ethylene oxide) is not expected at high levels. These types of compounds are generated in reactions as shown below:



It seems that these reactions have a higher incidence than those leading to the cleavage of the C-C bonds in the polyethylene sequences or even than in the cleavage of C-O bonds in poly(ethylene oxide) sequences.

Other polymers containing PEG fragments connecting specific groups with a polymeric matrix are known. Pyrolysis results for polystyrene with 4-benzyloxybenzyl alcohol groups bound to the backbone have been used for peptide synthesis (Wang resins) and were discussed in Section 6.2 (see Figure 6.2.15). Other copolymers have similarly crosslinking polyether bridges, such as poly(hydroxyethyl methacrylate-co-ethylene glycol dimethacrylate), etc.

- Other simple polyethers

Many other polyethers are used in practice either as homopolymers or in copolymers. Among these are poly(propylene glycol) or poly(propylene oxide) (the acronym PPO is used for this polymer and confusingly for other ones such as poly(phenylene oxide)) CAS# 25322-69-4, poly(oxetane) or poly(oxy-1,3-propylene) CAS# 25722-06-9, poly[oxy(hexyl-1,2-ethanediyl)] CAS # 25639-83-2, poly(1,4-oxyphenylene) CAS# 25667-40-7, poly(2,6-dimethyl-1,4-phenylene oxide) CAS# 25134-01-4, poly[oxy-(1-phenyl)ethylene] CAS# 25189-69-9, etc.

Poly(propylene oxide) is typically obtained by base catalyzed anionic polymerization of propylene oxide [12]. Both stereospecific and atactic forms are known. The polymer is used as a soft polyether unit in polyurethane elastomers and foams; in polymer electrolytes; as surfactants (lubricants, dispersants, antistatic agents, foam control agents) in printing inks, as solubilizers; in hydraulic fluids, coolant compositions; in various medical applications (protective bandages, drug delivery systems, organ preservation, dental compositions), etc.

Both poly(1,4-oxyphenylene) and poly(1,3-oxyphenylene) are temperature stable polymers and are used as high temperature stable fluids. Other poly(substituted oxyphenylenes) are also temperature stable and are used for purposes that require

stability in these conditions. Porous poly(2,6-dimethyl-1,4-phenylene oxide) is used as a sorbent phase (Tenax®) in chromatography.

Some reported results for the thermal decomposition of the polymers from this group are summarized in Table 9.1.7 [13].

TABLE 9.1.7. Summary regarding reports on the thermal decomposition of several polyethers [13].

Polymer	Temp. °C	Results	Ref.
poly(2,6-dimethyl-1,4-phenylene ether)	-	xylene, phenol, more complex fragments	14
poly(oxy-1,3-phenylene)	300–620	34% residue, 53% chain fragments, 13% volatiles comprising H ₂ O, CO, H ₂ , CH ₄ , CO ₂ , trace of C ₆ H ₆	15
poly(oxy-1,4-phenylene)	550	hydroquinone, phenol, benzene, diphenylether, 4,4'-dihydroxydiphenylether, 4-phenoxyphenol. In addition, a broad spectrum of phenyl and phenolic terminated oligomers with up to 10 aromatic units	16
poly(oxy-1,4-phenylene)	585	as 550° C plus, dibenzofuran and dibenzofuran-containing oligomers	16
poly(oxy-1,4-phenylene)	600	ether linkages decompose without rearrangement though cyclization to benzofuran systems	17
poly(oxy-1,4-phenylene)	350–620	decomposes to give H ₂ and methane	18
poly(oxy-2,5-dimethoxy-1,4-phenylene)	100–550	41% residue, 29% fragments, 30% volatiles comprising H ₂ , CH ₄ , CO, CO ₂ , CH ₃ OH, traces of H ₂ O, C ₂ H ₆ , other hydrocarbons	15
poly(oxy-2,6-dimethyl-1,4-phenylene)	100–550	26% residue, 66% chain fragments, 8% volatiles comprising of H ₂ , CH ₄ , H ₂ O, CO, CO ₂	15
poly(oxy-2,6-dimethyl-1,4-phenylene)	400–550	o-cresol, 2,6-dimethylphenol, 2,4-dimethylphenol, 2,4,6-trimethylphenol, various ketones, dimers, and more complicated structures, various combinations of the monomeric skeletons	19
poly(oxy-2-methylphenylene)	250–500	p-xylene, phenol, 2-methylphenol, 4-methylphenol, 2,4-dimethylphenol, and a variety of more complex structures	17
poly(oxybutylethylene)	321–365	mixture of saturated and hydrocarbons (C ₁ –C ₆), aldehydes (C ₁ –C ₆), H ₂ , H ₂ O	20
poly(oxypropylene) atactic	270–330	12.8% of products volatile at 25° C, including 4.00% acetaldehyde, 2.22% acetone, 1.43% dipropyl ether and 0.75% propylene	21
poly(oxypropylene) isotactic	275–355	20% of products volatile at 25° C, including 6.34% acetaldehyde, 2.39% acetone, 2.19% dipropyl ether, and 2.22% propylene	21
poly(oxytetra-methylene)	347	volatiles comprise a mixture of CH ₄ , C ₂ H ₆ , C ₃ H ₈ , C ₄ H ₁₀ , C ₂ H ₄ , C ₃ H ₆ , CH ₃ CHO, C ₂ H ₅ CHO, C ₃ H ₇ CHO	20
poly(propylene oxide)	-	PPO degrades via a random cleavage mechanism, the labile C-O bond scissions being preferred;	22
poly(propylene oxide- <i>alt</i> -allyl glycidyl ether)	300–400	heating resistant	23
poly(tetrahydrofuran)	175	compounds retaining one OH group at one end, and ethyl ether, propyl ether, butyl ether or aldehyde at the other end	24

Results for a Py-GC/MS analysis of a poly(propylene glycol) sample, CAS# 25322-69-4, with $M_n = 345$ and the structure $H[-O-CH(CH_3)CH_2]_n-OH$ are shown in Figure 9.1.10. The pyrolysis was done in similar conditions as for other examples, at 600° C in He at a heating rate of 20° C/ms. with 10 s THT. The separation was done on a Carbowax column with the GC starting at 40° C with a ramp of 2° C/min. up to 240° C and a final oven time of 20 min. (see Table 4.2.2).

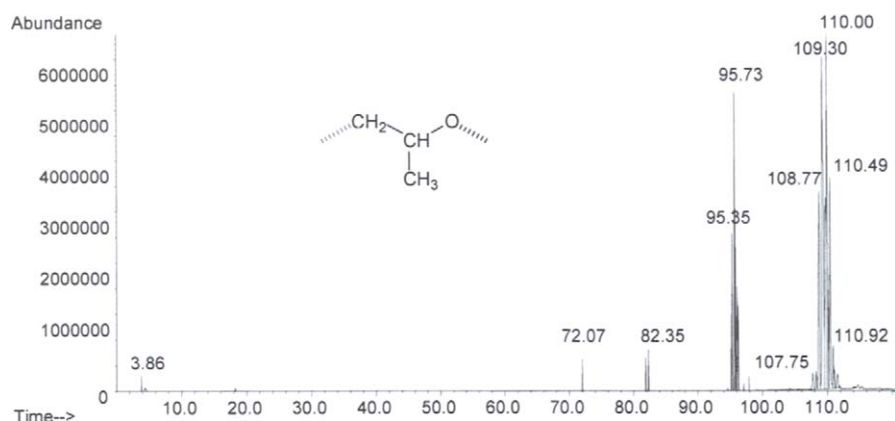


FIGURE 9.1.10. Result for a Py-GC/MS analysis of poly(propylene glycol) $M_n = 345$. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

The comparison of the pyrogram from Figure 9.1.10 with the pyrograms for PEG shows obvious differences. The peak identification for the pyrogram from Figure 9.1.10 is given in Table 9.1.8.

TABLE 9.1.8. Compounds identified in the pyrogram of poly(propylene glycol) $M_n = 345$ as shown in Figure 9.1.10.

Peak	Compound*	Ret. Time	MW	Area %
1	1-propene	4.44	42	trace
2	acetaldehyde	5.86	44	trace
3	propanone	7.93	58	trace
4	diisopropylether	20.20	102	trace
5	1-(1-methylethoxy)-2-propanone	25.65	116	trace
6	1-[1-methyl-2-(2-propenyloxy)ethoxy]-2-propanol	56.53	174	trace
7	2,6-bis(<i>tert</i> -butyl)-4-methylphenol (BHT antioxidant)	72.07	220	0.62
8	2-(2-hydroxypropoxy)propan-1-ol	81.94	134	0.83
9	2-(2-hydroxypropoxy)propan-1-ol diastereoisomer	82.35	134	0.84
10	2-[2-(2-hydroxypropoxy)propoxy]propan-1-ol	95.21	192	1.60
11	2-[2-(2-hydroxypropoxy)propoxy]propan-1-ol diastereoisomer	95.35	192	4.13
12	2-[2-(2-hydroxypropoxy)propoxy]propan-1-ol diastereoisomer	95.73	192	8.14
13	2-[2-(2-hydroxypropoxy)propoxy]propan-1-ol diastereoisomer	95.84	192	3.59
14	1-[1-methyl-2-(1-methyl-2-prop-2-enyloxyethoxy)-ethoxy]propan-2-ol	96.07	232	3.85
15	1-[1-methyl-2-(1-methyl-2-prop-2-enyloxyethoxy)-ethoxy]propan-2-ol diastereoisomer	96.11	232	0.68
16	1-[1-methyl-2-(1-methyl-2-prop-2-enyloxyethoxy)-ethoxy]propan-2-ol diastereoisomer	96.17	232	0.68
17	1-[1-methyl-2-(1-methyl-2-prop-2-enyloxyethoxy)-ethoxy]propan-2-ol diastereoisomer	96.30	232	0.68
18	4,7,10-trimethyl-2,5,8,11-tetraoxatetradecan-13-ol	97.12	264	0.13
19	2-[2-[2-(2-hydroxypropoxy)propoxy]propoxy]propan-1-ol	107.75	250	0.78

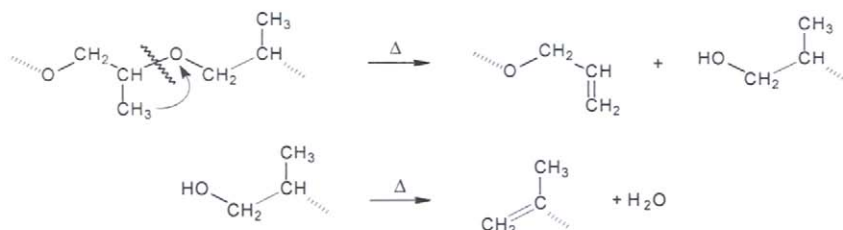
* Note: some peak assignments are tentative only.

TABLE 9.1.8 (continued). Compounds identified in the pyrogram of poly(propylene glycol) $M_n = 345$ as shown in Figure 9.1.10.

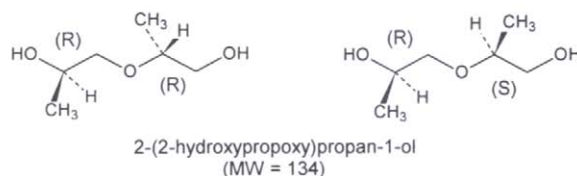
Peak	Compound*	Ret. Time	MW	Area %
20	2-{2-[2-(2-hydroxypropoxy)propoxy]propoxy}propan-1-ol diastereoisomer	108.28	250	0.75
21	2-{2-[2-(2-hydroxypropoxy)propoxy]propoxy}propan-1-ol diastereoisomer	108.77	250	9.06
22	2-{2-[2-(2-hydroxypropoxy)propoxy]propoxy}propan-1-ol diastereoisomer	109.30	250	23.74
23	2-{2-[2-(2-hydroxypropoxy)propoxy]propoxy}propan-1-ol diastereoisomer	109.77	250	10.00
24	2-{2-[2-(2-hydroxypropoxy)propoxy]propoxy}propan-1-ol diastereoisomer	110.00	250	14.53
25	2-{2-[2-(2-hydroxypropoxy)propoxy]propoxy}propan-1-ol diastereoisomer	110.18	250	3.22
26	1-{1-methyl-2-[1-methyl-2-(1-methyl-2-prop-2-enyloxy-ethoxy)ethoxy]ethoxy}propan-2-ol	110.49	290	9.12
27	1-{1-methyl-2-[1-methyl-2-(1-methyl-2-prop-2-enyloxy-ethoxy)ethoxy]ethoxy}propan-2-ol diastereoisomer	110.92	290	1.54
28	1-{1-methyl-2-[1-methyl-2-(1-methyl-2-prop-2-enyloxy-ethoxy)ethoxy]ethoxy}propan-2-ol diastereoisomer	111.10	290	0.66
29	1-{1-methyl-2-[1-methyl-2-(1-methyl-2-prop-2-enyloxy-ethoxy)ethoxy]ethoxy}propan-2-ol diastereoisomer	111.60	290	0.83

* Note: some peak assignments are tentative only.

The results shown in Table 9.1.8 seem to indicate that the main reaction that takes place during poly(propylene oxide) pyrolysis is the cleavage of C–O bond and that there is very little C–C bond cleavage. Some elimination of water from the resulting alcohol is also possible. These reactions are shown below:



Some of the fragments generated from poly(propylene oxide) pyrolysis contain asymmetric carbon atoms. For example, isomer compounds with two chiral centers are shown below in (R,R) and (R,S) forms:



The above two diastereoisomers will give two peaks in the pyrogram (at 81.94 min. and 82.35 min.). The next group of peaks in the pyrogram is formed by the compounds with three chiral centers. These compounds elute in the chromatogram between 95.0 min. and 97.0 min. The part of the pyrogram given in Figure 9.1.10 situated between retention time 94 min. and 112 min. is shown in Figure 9.1.11.

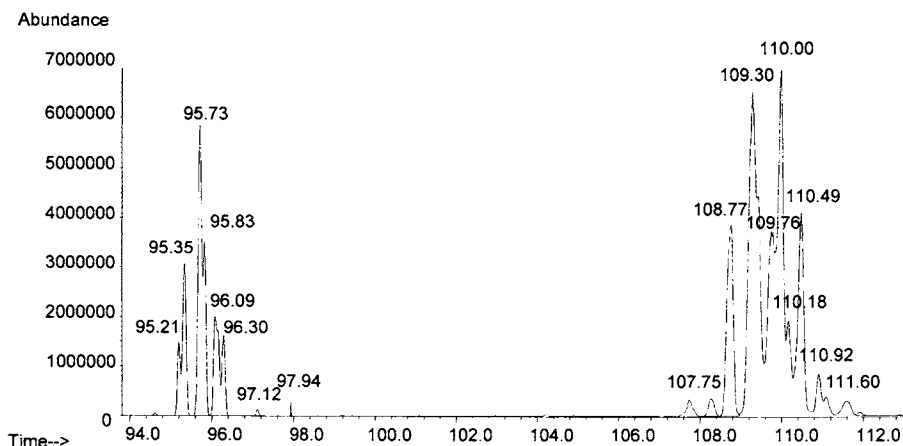
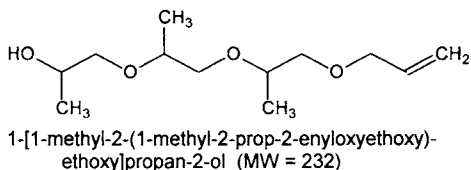
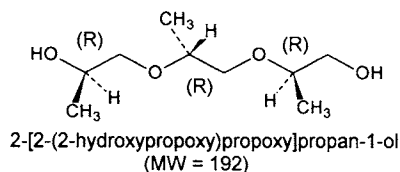


FIGURE 9.1.11. Peaks in the retention time interval 94 min. to 112 min. from Figure 9.1.10 of poly(propylene glycol) pyrogram.

Eight different compounds can be distinguished in the first group of peaks shown in Figure 9.1.11. These peaks are generated by two different sets of diastereoisomers each with four components. The tentatively assigned structures for one compound from each set are indicated below:



The compound with MW = 232 also can be 1-{1-methyl-2-[1-methyl-2-(methylvinyl)oxy]ethoxy}ethoxy}propan-2-ol. More than one set of diastereoisomers was assigned to the peaks eluting between 95.0 min. and 97.0 min. since the spectra of the diastereoisomers should be identical, while the compounds generating the peaks in the time range 95.0 min. to 97.0 min. have two different spectra (although rather similar), as shown in Figure 9.1.12.

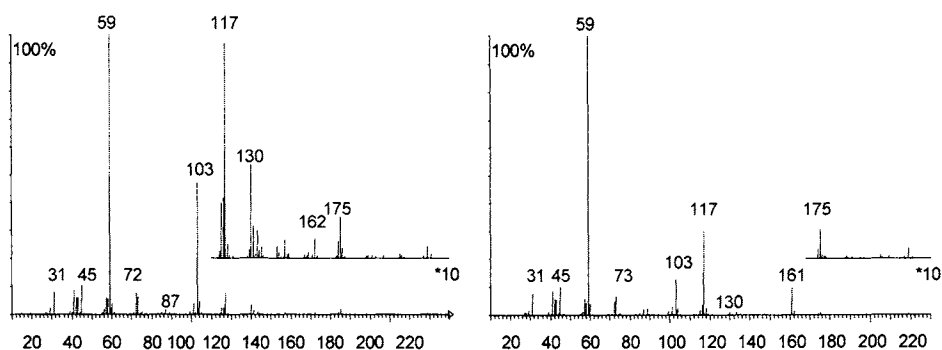
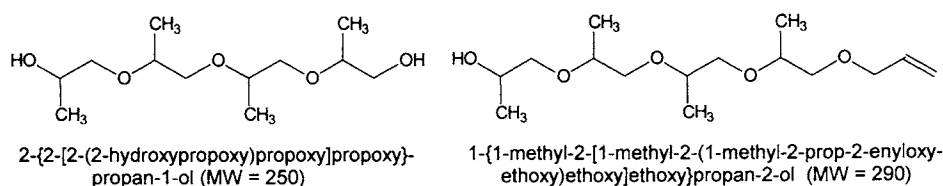


FIGURE 9.1.12. Spectra assigned to 2-[2-(2-hydroxypropoxy)propoxy]propan-1-ol and to 1-[1-methyl-2-(1-methyl-2-prop-2-enyloxyethoxy)ethoxy]ethoxy]propan-2-ol, both eluting in the same region of the chromatogram.

The next group of peaks eluting between 107.0 min. and 112.00 min. and shown in Figure 9.1.12 is generated by the compounds of the type:



These compounds have four chiral centers and each one generates eight diastereoisomers. The resulting 16 peaks are not well separated in the chromatogram shown in Figure 9.1.11.

A study on thermal degradation and the effects of heating rate on poly(propylene oxide) (PPO) using only Py-MS was reported in literature [25]. It was determined that PPO degrades via a random cleavage mechanism, the C–O bonds being weaker than C–C bonds, which is in agreement with the results suggested by the composition of pyrolysate given in Table 9.1.8.

A similar observation regarding bond cleavage can be noticed during the pyrolysis of poly(tetramethyleneglycol) or poly(1,4-butandiol) or poly(tetrahydrofuran) or α -hydro- ω -hydroxy-poly(oxy-1,4-butandiol) CAS# 25190-06-1. This polymer is typically found in copolymers forming “soft segments” in the polymer chain, necessary in some elastomeric materials. The pyrogram obtained in similar conditions as for other examples previously discussed (see Table 4.2.2) is given for a poly(tetrahydrofuran) sample with $M_n = 250$ in Figure 9.1.13.

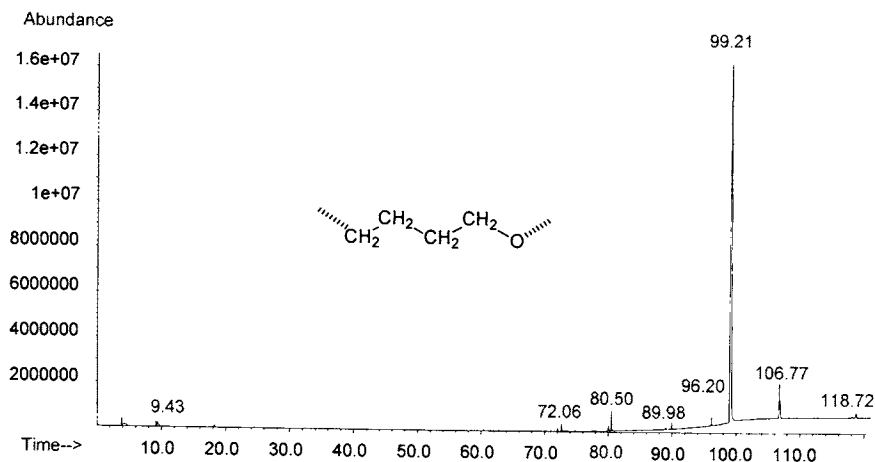


FIGURE 9.1.13. Result for a Py-GC/MS analysis of poly(tetramethyleneglycol) or poly(tetrahydrofuran) $M_n = 250$. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

The main peak in the pyrogram was tentatively assigned to 4-(4-hydroxybutoxy)butan-1-ol with the spectrum shown in Figure 9.1.14.

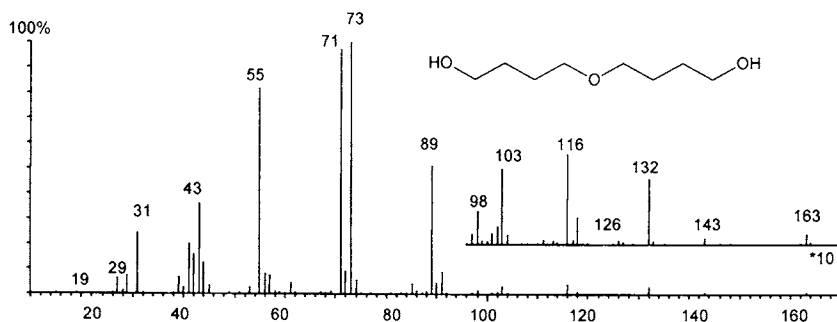


FIGURE 9.1.14. Mass spectrum tentatively assigned to 4-(4-hydroxybutoxy)butan-1-ol ($MW = 162$).

The presence of this main compound indicates that the C–C bonds are relatively stable compared to C–O bonds. The other peaks in the chromatogram correspond to other related compounds such as 1,4-butanediol, or compounds resulting from the water elimination at the end OH groups of larger fragments of the polymer. This is a rather different behavior compared to that of PEG, where several types of bonds can be cleaved, generating the variety of compounds shown in Table 9.1.1. The differences in the bond stability seem to influence this result. On the other hand, for the case of poly[butylene terephthalate-co-poly(butylene glycol) terephthalate] pyrolysis (see Section 10.1, Figure 10.1.8), poly(butylene glycol) sequences generate segments

similar to those generated from PEG, but containing four carbons instead of two carbons.

Another polymer containing ether bond is poly[(dibenzo-18-crown-6)-co-formaldehyde] CAS# 53660-42-7. Pyrolysis results for this polymer obtained in similar conditions as for other examples, at 600° C in He at a heating rate of 20° C/ms. with 10 s THT (see Table 4.2.2), are given in Figure 9.1.15.

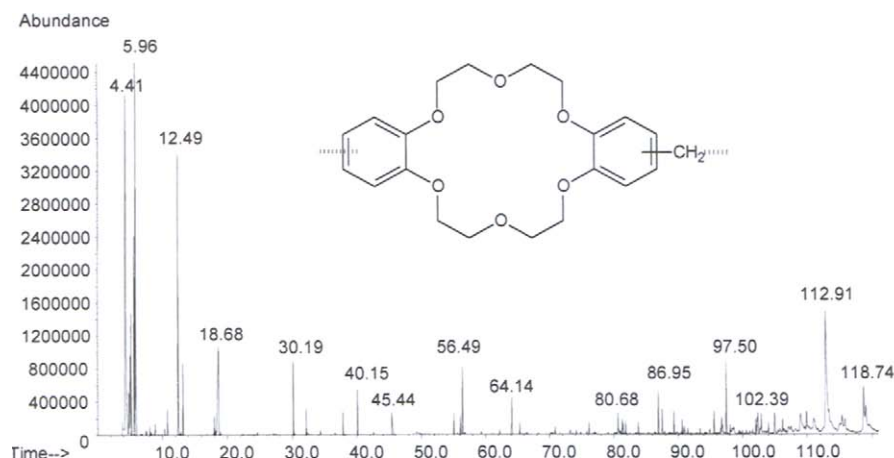


FIGURE 9.1.15. Result for a Py-GC/MS analysis of poly[(dibenzo-18-crown-6)-co-formaldehyde]. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

The peak identification for the pyrogram from Figure 9.1.15 was done using mass spectral library searches only and is given in Table 9.1.9.

TABLE 9.1.9. Compounds identified in the pyrogram of poly[(dibenzo-18-crown-6)-co-formaldehyde] as shown in Figure 9.1.15.

Peak	Compound	Ret. Time	MW	Area %
1	ethene	4.41	28	19.38
2	methoxyethane	4.92	60	0.87
3	formaldehyde	5.11	30	3.07
4	diethyl ether	5.25	74	3.34
5	ethyl vinyl ether	5.76	72	5.95
6	acetaldehyde	5.97	44	12.77
7	propanone	8.16	58	0.21
8	propenal (acrolein)	8.95	56	0.35
9	2-butanone	10.83	72	0.57
10	ethanol	12.49	46	8.05
11	2-methyl-1,3-dioxolane	13.25	88	1.74
12	2-butenal	18.03	70	0.46
13	water	18.68	18	5.93
14	1-(2-ethoxyethoxy)ethene	21.07	116	trace

TABLE 9.1.9 (continued). Compounds identified in the pyrogram of poly[(dibenzo-18-crown-6)-co-formaldehyde] as shown in Figure 9.1.15.

Peak	Compound	Ret. Time	MW	Area %
15	2-methoxyethanol	27.11	76	trace
16	2-ethoxyethanol	30.19	90	1.84
17	2-propyl-1,3-dioxolane ?	37.87	116	0.52
18	2-(ethenyloxy)ethanol	40.15	88	1.04
19	acetic acid	45.44	60	0.82
20	formic acid	49.26	46	0.82
21	4-hydroxy-3-methylacetophenone	55.11	150	0.57
22	1,2-ethandiol monoformate	56.13	90	0.51
23	1,2-ethandiol	56.49	62	2.14
24	1,2-ethandiol monoacetate	56.82	104	trace
25	2'-hydroxy-4',5'-dimethylacetophenone	64.14	164	1.06
26	p-isopropylbenzaldehyde	65.36	146	0.30
27	2,2'-oxybisethanol	75.82	106	trace
28	3,5-dimethyl-4-hydroxybenzaldehyde	76.17	150	0.35
29	2,5-dimethylphenol	80.68	122	0.54
30	3-methylphenol	81.35	108	0.44
31	1-ethoxy-2-methyl-5-ethylbenzene ?	81.49	164	0.32
32	4-ethyl-2-methoxyphenol	81.86	152	0.37
33	2-ethyl-5-methylphenol	83.82	136	0.33
34	2,4,5-trimethylphenol	86.95	136	1.21
35	2,4-dimethylphenol	87.57	122	0.75
36	2-methyl-5-(1-methylethyl)phenol	89.38	150	0.68
37	2-(2-methoxyethoxy)-4,5-dimethylphenol	90.67	196	0.40
38	2,4,6-trimethylphenol	95.61	136	0.71
39	1,2-dihydroxy-4,5-dimethylbenzene	96.78	138	0.26
40	2-(2-ethoxyethoxy)-4,5-dimethylphenol	97.50	210	1.93
41	2-methoxy-4-(1-propenyl)phenol	102.09	164	0.48
42	2-methyl-1,3-benzenedicarboxaldehyde	102.39	148	1.04
43	4,5-dimethyl-2-vinyloxyphenol	105.00	164	0.95
44	1,2-benzenediol	106.24	110	0.41
45	1,3-benzenediol	108.99	110	1.14
46	3-methyl-1,2-benzenediol	112.91	124	11.25
47	2-(2-hydroxyethoxy)-4-methylphenol ?	118.74	168 ?	2.73
48	2-(2-hydroxyethoxy)-5-methylphenol ?	119.07	168 ?	1.40

The composition of the pyrolysate as shown in Table 9.1.9 indicates that it contains some compounds generated from the aliphatic ether moiety, some compounds generated by the cleavage of the O—C bond retaining the oxygen atom to the benzene ring, and some generated from the cleavage of the C—C bonds between the CH₂ groups and the aromatic rings. This leads to the formation of several compounds such as 1-(2-ethoxyethoxy)ethene, 2-ethoxyethanol, 1,3-benzenediol, 3-methyl-benzene diol, and 3-methylphenol. Some compounds in Table 9.1.9 were identified only tentatively, since their mass spectrum was not available. Among these compounds is 2-(2-ethoxyethoxy)-4,5-dimethylphenol, to which was assigned the spectrum shown in Figure 9.1.16.

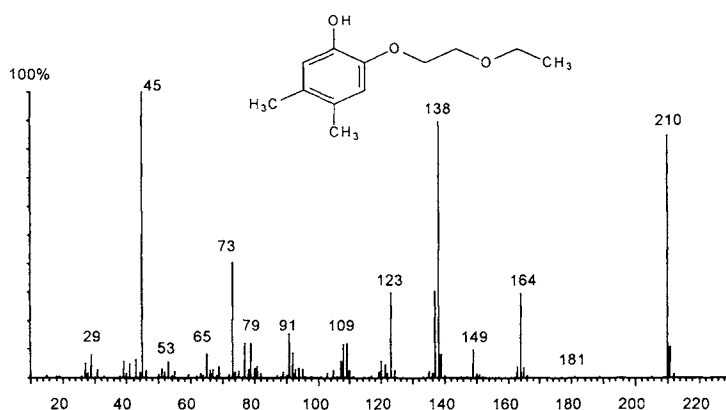


FIGURE 9.1.16. Mass spectrum tentatively assigned to 2-(2-ethoxyethoxy)-4,5-dimethylphenol.

Other peaks in the pyrogram were even more difficult to identify, such as those which possibly belong to 2-(2-hydroxyethoxy)-4-methylphenol or 2-(2-hydroxyethoxy)-5-methylphenol and elute at 118.74 and 119.07 min. in the pyrogram shown in Figure 9.1.15.

Pyrolysis of poly(2,6-dimethyl-1,4-phenylene oxide) [$-\text{C}_6\text{H}_2(\text{CH}_3)_2\text{O}-$] $_n$, CAS# 25134-01-4, is further discussed for a sample with $M_w = 244,000$. The experimental conditions used to generate the pyrogram shown in Figure 9.1.17 were similar to those for other previous examples (see Table 4.2.2). Peak identification for the pyrogram was done using mass spectral library searches only and is given in Table 9.1.10 and Table 9.1.11.

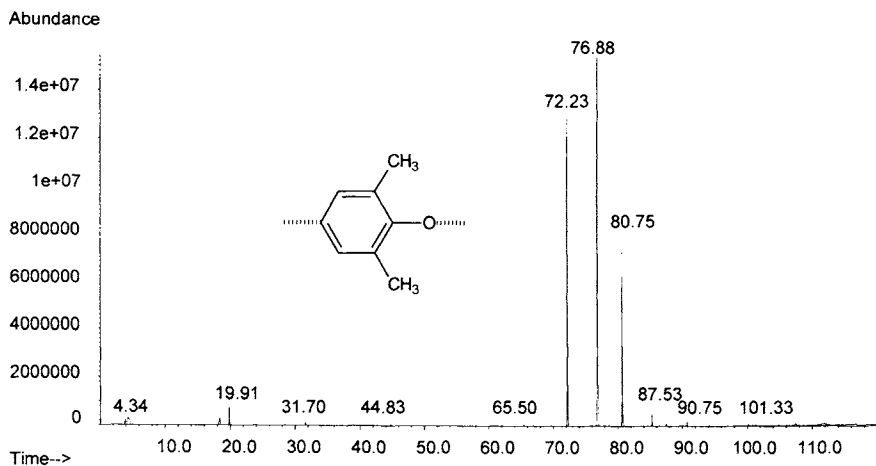


FIGURE 9.1.17. Result for a Py-GC/MS analysis of poly(2,6-dimethyl-1,4-phenylene oxide) $M_w = 244,000$. Pyrolysis done on 0.4 mg material at 600° C, with the separation on a Carbowax type column.

TABLE 9.1.10. *Compounds identified in the pyrogram of poly(2,6-dimethyl-1,4-phenylene oxide) $M_w = 244,000$ as shown in Figure 9.1.17.*

Peak	Compound	Ret. Time	MW	Area %
1	carbon dioxide	4.33	44	0.86
2	butane	4.48	58	1.40
3	water	18.46	18	1.12
6	1,3,5-trimethylbenzene	31.70	120	0.41
7	1,2,3,5-tetramethylbenzene	44.83	134	0.27
12	2,6-dimethylphenol	72.23	122	30.92
13	2,4,6-trimethylphenol	76.89	136	40.06
14	2-methylphenol	76.94	108	trace
15	phenol	77.12	94	0.16
16	3,5-dimethylphenol	80.75	122	18.56
17	3,4-dimethylphenol	85.31	122	1.46
18	3,4,5-trimethylphenol	87.53	136	0.34
19	2-(2,6-dimethylphenoxy)-1,3,5-trimethylbenzene	90.75	240	0.73
20	2-(2,4,6-trimethylphenoxy)-1,3,5-trimethylbenzene	101.33	254	0.22

In addition to the alkylbenzenes and the phenols indicated in Table 9.1.10, traces of a series of nitrogen containing compounds were detected in the pyrolysate. These compounds obviously have a different origin than the pyrolysate of pure polymer. The list of these compounds is given in Table 9.1.11.

TABLE 9.1.11. *Trace nitrogenous impurity compounds identified in the pyrogram of a sample of poly(2,6-dimethyl-1,4-phenylene oxide) $M_w = 244,000$ as shown in Figure 9.1.17.*

Peak	Compound	Ret. Time	MW	Area %
4	N-butylidene-1-butanamine (impurity)	19.91	127	2.31
5	N,N-dibutyl-1-butanamine(impurity)	28.49	185	0.16
8	N,N-dibutylformamide (impurity)	65.50	157	0.36
9	N,N-dibutylacetamide (impurity)	67.00	171	0.23
10	N,N-dibutylpropionamide (impurity)	67.27	185	0.22
11	N,N-dibutylbutyramide (impurity)	69.68	199	0.22

Note: the area percent shown in Table 9.1.11 is given relative to all identified compounds in the pyrogram.

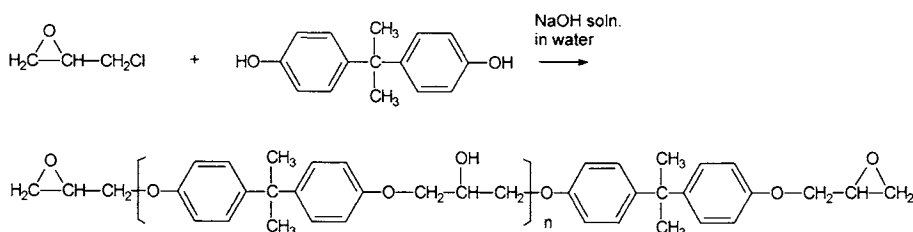
As seen from Table 9.1.10, besides 2,6-dimethylphenol and 3,5-dimethylphenol, which are expected to be generated in the pyrogram, trimethyl phenols are also present at considerable levels. Also trimethylbenzene and even tetramethylbenzene were detected in the pyrolysate. The polymer being relatively stable at elevated temperatures, the decomposition starts only above 450° C when migration of the -CH₃ groups seems to occur.

- Polyethers used in epoxy resins

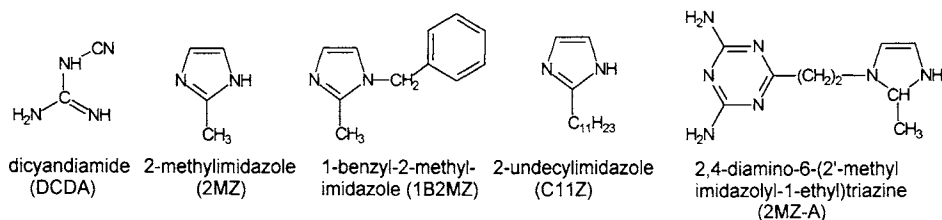
Since epoxides are reactive compounds, the epoxy groups present in pre-polymers are used for crosslinking or "curing" purposes. Curing occurs when the pre-polymer is treated with a suitable multi-functional crosslinking agent, or with an accelerator. The

crosslinking agent, such as a polyamine, reacts with the epoxy end-groups, linking them together to form a tridimensional network of polymer chains. The accelerator facilitates the crosslinking of the pre-polymer through its epoxy groups and does not form itself bridges between the pre-polymer units. Various new bonds are formed in these reactions, the most common group in the final polymer remaining the ether. In addition, hydroxyl groups are frequently formed in these materials. The formation of numerous hydroxyl groups in the polymer leads to excellent adhesion properties of the epoxy resins to many surfaces. This allows the use of these materials as coatings, adhesives, and polymeric constituent in many composites.

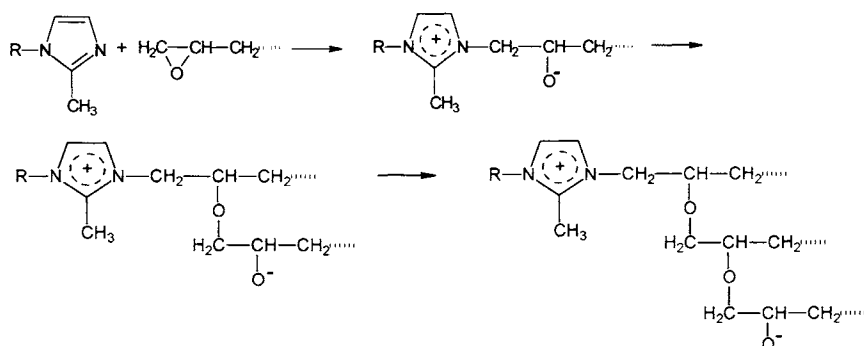
The pre-polymers typically contain at least two epoxy groups spaced with an aromatic or aliphatic backbone or even by a fragment of chain including other functionalities. The most commonly used resin from this class is probably formed from epichlorohydrin and bisphenol A or 4-[1-(4-hydroxy-phenyl)-isopropyl]phenol under basic conditions to give a polymeric diglycidyl polyether as shown below:



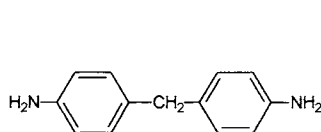
The reaction of this polymer may continue with several additions of bisphenol A units opening the epoxy rings to give short chains of up to 20 repeat units, still terminated with epoxy groups. The resulting material can have various DP and can be solid or a viscous liquid. This product is further "cured" by the crosslinking of the polymeric chains. Lewis acid catalysts such as imidazole derivatives or BF_3 ethylamine complex can be used for generating crosslinking by opening the epoxy groups and formation of ether bridges, which leads to the hardening of the resin. The structures of several accelerators used as hardeners are shown below:



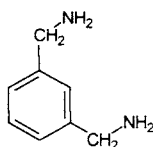
The mechanism of curing of the epoxy pre-polymer using, for example, imidazole derivatives is indicated schematically by the following reactions:



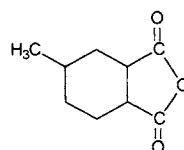
Compounds such as polyamines, polysulfides, urea, acids, anhydrides, etc. can be used to react either at the epoxy group or at both epoxy and hydroxy groups, forming bridges and a thermorigid polymer. Sometimes these crosslinking reagents are used with the addition of an accelerator such as tertiary amines. The structures of several compounds used for crosslinking are shown below:



diphenyldiaminomethane
(DDM)



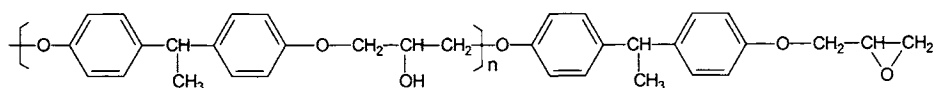
m-xylenediamine



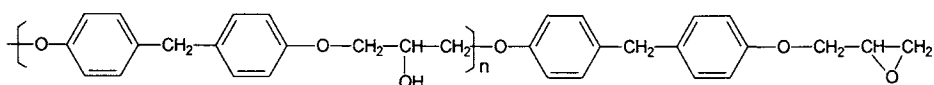
methylhexahydrophthalic
anhydride (MeHHPA)

Other crosslinking reagents include hexahydrophthalic anhydride, 4,4'-diaminodiphenylsulfone, 4,4'-diaminodiphenylether, triethylenetetramine, norbornyl dianhydride siloxane, etc.

Other phenol derivatives that are used to form the backbone of an epoxy resin include bisphenol E, bisphenol F, resorcinol, brominated bisphenols, and more highly functionalized molecules such as tetrakisphenylolethane. Alcohols, amines, and carboxylic acids may be combined with epichlorohydrin to give a range of diglycidyl ether based epoxy resins. Non-aromatic, commercially available epoxides are produced by peracid epoxidation of alkenes and dienes, such as vinyl cyclohexene and esters of cyclohexane carboxylic acids [23]. The chemical formulas for two common uncured polymers are shown below:

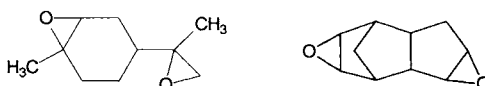


Poly[bisphenol E bis(oxiranylmethyl) ether]



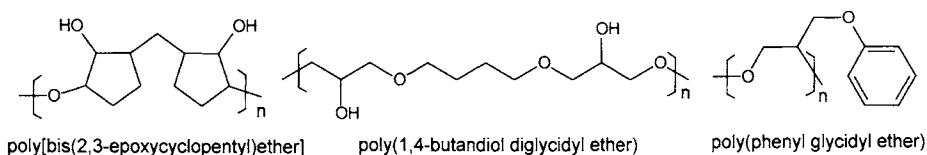
Poly[bis(bisphenol F bis(oxiranylmethyl) ether)]

Small molecule epoxides, and some epoxy oligomers also are used as reactive diluents, mixing them with other polymers for crosslinking purposes. An example of epoxide used as curing additive is poly(limonene dioxide) or poly[1-methyl-4-(2-methyloxiranyl)-7-oxabicyclo[4.1.0]heptane], CAS# 29616-43-1. This compound can form ether bonds upon heating or by photoinduction in the presence of aryl substituted sulfonium salts. Poly(dicyclopentadiene dioxide), CAS# 29987-76-6, has similar properties. The idealized structure of the two monomers with the intact epoxy groups are shown below:



Thermal decomposition of the cured resins containing ether groups form small molecules containing fragments mainly generated by the cleavage of the C–O bonds. A considerable number of studies on thermal stability of curable resin ethers were reported in literature [23, 26–41] (see also Section 8.3). Resins such as poly(bisphenol A diglycidyl ether) and poly(bisphenol F diglycidyl ether) were thoroughly studied since they have many practical applications, for example in coatings, in polymer sheets used for flooring and other structural laminates, in adhesives, etc. The decomposition temperature of the material depends on the curing agent. For example, poly(bisphenol A diglycidyl ether) cured with hexahydrophthalic anhydride has a decomposition temperature of about 392° C, and the polymer cured with 2-methylimidazole decomposes at about 420° C. The polymer shows 6.8% weight loss (triethylene-tetramine cured), 5.5% weight loss (4,4'-methylenedianiline cured), 5% weight loss (Versamide cured) after heating at 210° C for 300 h [42]. Poly(bisphenol A diglycidyl ether) is available under various commercial names and may have several additives that modify its mechanical properties, electrical properties, or thermochemical properties. Thermal decomposition of these products also may vary depending on the presence of specific additives [43–45].

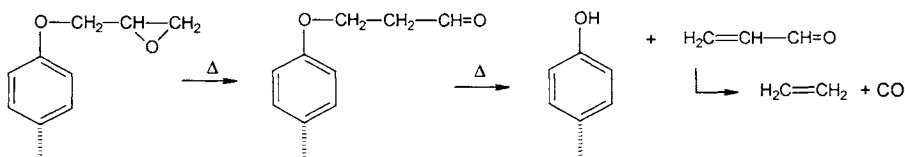
The polyether poly(bisphenol F diglycidyl ether) shows a weight loss as low as 80° C in NaOH [23]. Some other polyethers are described in literature, such as poly[bis(2,3-epoxy-cyclopentyl)ether], poly(1,4-butandiol diglycidyl ether), poly(phenyl glycidyl ether), poly(1,2-epoxy-3-phenoxypropane), etc. The structures of the main sequence of these polymers after curing are shown below:



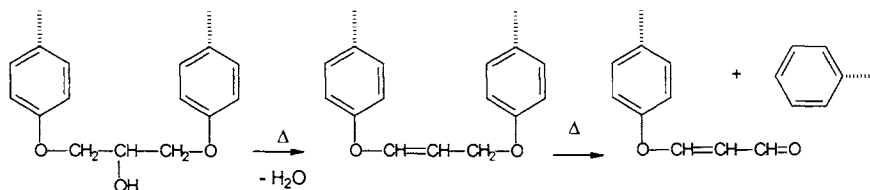
Poly[bis(2,3-epoxycyclopentyl)ether] cured with phenylenediamine decomposes slowly

upon heating in air at 212° C, showing about 10% loss after 2 h of heating [46]. For most polyethers the C–O bonds break upon heating more easily than the C–C bonds.

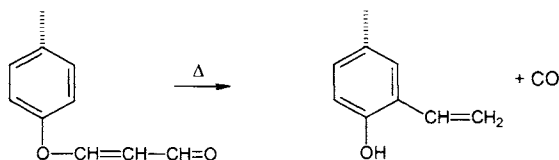
Various schemes were proposed for the thermal decomposition of epoxides (see e.g. [47]). One decomposition path starts with the residual epoxide groups, which under the influence of heat can undergo reactions as shown below:



Similar reactions can occur in the middle of the epoxide backbone, the cleavage taking place with a higher probability at a C–O bond as shown below:



The unsaturated aldehyde end groups can further decompose in reactions of Claisen rearrangement type:



The variety of compounds that can result from the polymer pyrolysis as well as the typically complex structure of the epoxy resins make the interpretation of the results of pyrolysis of epoxy resins rather difficult. Several results regarding pyrolysis of epoxy resins that were reported in literature are shown in Table 9.1.12 [13].

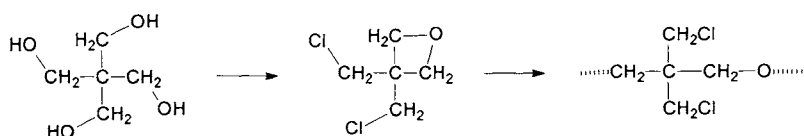
TABLE 9.1.12. Summary regarding reports on pyrolysis of several epoxy resins [13].

Polymer	Curing agent	Temp °C	Results	Ref.
bisphenol A epoxy resin	various hardeners	-	phenol, cresols, bisphenol A, fragments generated from bisphenol A	48
diglycidyl ether of bisphenol A	4,4'-diaminodiphenyl methane	600	phenol, cresols, bisphenol A, bisphenol A ether with one glycidyl group, bisphenol A ether with two glycidyl groups, compounds related to the curing reagent such as {4-[(4-aminophenyl)methyl]phenyl}methylaniline, {4-[(4-aminophenyl)methyl]phenyl}dimethylamine, etc	49
diglycidyl ether of bisphenol A	1-benzyl-2-methylimidazole	600	phenol, cresols, bisphenol A, bisphenol A ether with one glycidyl group, bisphenol A ether with two glycidyl groups, other fragments related to bisphenol A, etc.	49
diglycidyl ether of bisphenol A	<i>m</i> -xylenediamine	600	phenol, cresols, bisphenol A, other fragments related to bisphenol A	49
diglycidyl ether of bisphenol A	methylhexahydro-phthalic anhydride	600	compounds related to methylhexahydro-phthalic anhydride, bisphenol A, hexahydrophthalic anhydride, methylhexahydro-phthalic anhydride, etc.	49
diglycidyl ether of bisphenol A	dicyanodiamide, etc.	700	various aromatic amines and phenols	50
epoxy-novolac	dicyanodiamide + substituted urea	700	aniline, phenol, 2-methylphenol, 4-methylphenol, 2,6-dimethylphenol, 2-ethylphenol, 2,4-dimethylphenol, 4,7-dimethylbenzofurane, 9(H)-xanthene, 2-[(4-hydroxy-phenyl)methyl]phenol, 4,4'-dihydroxydiphenylmethane, 5-methyl-1-(4-methylphenyl)-2-benzimidazolinone, 2,3-dihydro-3-methyl-1-phenyl-4(1H)-quinazolinone	51
N,N,N',N'-tetraglycidyl-4,4'-diaminodiphenylmethane	4,4'-diamino-diphenylsulfone	700	aniline, phenol, N-methylaniline, 4-methylaniline, N,N'-dimethylaniline, N-ethylaniline, N,4-dimethylaniline, N,N-4-trimethylaniline, isoquinoline, 3(4)-methylquinoline, 1H-indole, 2-ethylquinoline, 6(8)-methylquinoline, 4,4'-diaminodiphenylmethane, dimethylbenzidine	51
N,N,N',N'-tetraglycidyl-4,4'-diaminodiphenylmethane	3-(3,4-dichlorophenyl)-1,1-dimethylurea (DIURON)	700	various aromatic amines	50
tetrahydroxytetraphenyl ethane diglycidyl ether	methylhexahydro-phthalic anhydride	600	phenol, cresol, compounds related to methylhexahydro-phthalic anhydride	49
tetrahydroxytetraphenyl ethane diglycidyl ether	4,4'-diaminodiphenyl methane	600	phenol, cresol, compounds related to 4,4'-diaminodiphenylmethane	49

As indicated in Table 9.1.12, in the case of using crosslinking reagents (and not only accelerators), fragments of these compounds are seen in the pyrograms together with fragments of the main chain of the epoxy resin. This is also related to the content of crosslinking reagent used in the polymer. Some epoxy resins use large proportions of curing agent in the material.

- Halogenated poly(ethers)

A number of chlorinated poly(ethers) have practical uses. A common compound from this group is polyepichlorohydrin, $[-CH(CH_2Cl)CH_2O-]_n$. Polyepichlorohydrin has practical applications as an elastomer and is used in copolymers with propylene oxide, ethylene oxide, allyl glycidyl ether (1-allyloxy-2,3-epoxypropane), etc. Another example is poly{oxy[2,2'-bis(chloromethyl)-1,3-propanediol]} or poly[oxy-1,3-(2,2'-dichloromethyl)propylene], CAS# 25323-58-4, which can be used as inert lining material for chemical plant equipment, as adhesive, coating material, etc. This macromolecule can be prepared starting with pentaerythritol in the sequence of reactions shown below:



This polymer has higher thermal stability than polymers having a hydrogen in β -position to chlorine, which readily eliminate HCl during heating.

A pyrogram for poly(epichlorohydrin), CAS# 24969-06-0, with $M_w = 700,000$ is shown in Figure 9.1.18. The pyrolysis was done similarly to other examples previously discussed, at 600°C in He at a heating rate of 20°C/m . The separation was done on a Carbowax column (see Table 4.2.2). The peak identification was done using MS spectral library searches and the results are given in Table 9.1.13.

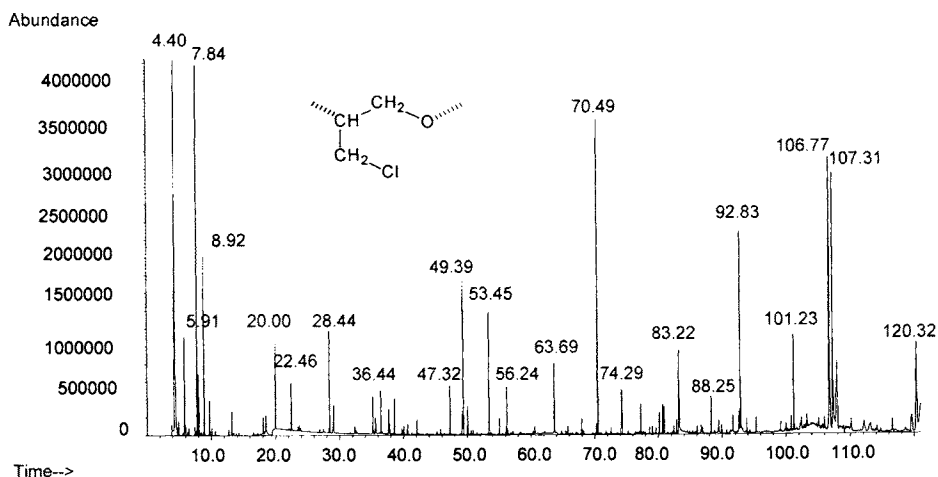


FIGURE 9.1.18. Result for a Py-GC/MS analysis of polyepichlorohydrin $M_w = 700,000$. Pyrolysis done on 0.4 mg material at 600°C , with the separation on a Carbowax type column.

TABLE 9.1.13. Compounds identified in the pyrogram of polyepichlorohydrin $M_w = 700,000$ as shown in Figure 9.1.18.

Peak	Compound	Ret Time	MW	Area %
1	carbon monoxide	4.32	28	1.22
2	propene	4.40	42	5.03
3	1,3-butadiene	4.98	54	0.44
4	acetaldehyde	5.91	44	2.57
5	1,3-cyclopentadiene	6.56	66	0.50
6	propanal	7.47	58	0.40
7	2-chloro-1-propene	7.84	76	4.74
8	propanone (acetone)	8.10	58	1.09
9	2-propenal	8.92	56	2.56
10	2-methylfuran	9.74	82	0.62
11	2-methylpropenal	10.11	70	0.23
12	3-methylfuran	10.62	82	trace
13	benzene	12.72	78	0.25
14	2,5-dimethylfuran	13.22	96	0.60
15	2-methy-1,3-dioxolane	13.57	88	trace
16	2,4-dimethylfuran	13.94	96	trace
17	2-pentanone	14.35	86	0.24
18	3-methyl-3-buten-2-one	15.24	84	trace
19	toluene	18.08	92	trace
20	1,2-dichloropropane	18.08	112	0.89
21	water	18.53	18	1.11
22	hydrochloric acid	19.92	36	4.40
23	phenol	20.00	94	2.47
24	2-propen-1-ol	22.46	58	1.30
25	3-penten-2-one	23.57	84	trace
26	5-hexen-2-one	23.74	98	0.43
27	1,3-dichloro-1-propene	23.92	110	trace
28	5-methyl-3-hexen-2-one	26.90	112	0.36
29	2-methylbutyloxirane ?	28.44	114	2.09
30	1-chloro-2-propanone	29.05	92	0.95
31	vinyl crotonate ?	32.38	112	0.51
32	3-chloro-1-vinyloxypropan-2-ol	35.19	136	1.22
33	1-hydroxy-2-propanone	35.62	74	1.16
34	4-(chloromethyl)-2,2-dimethyl-1,3-dioxolane	35.80	150	trace
35	1-chloro-2-propanol	36.44	94	2.61
36	2-(chloromethyl)tetrahydropyran	37.67	134	0.73
37	3-(chloromethyl)tetrahydropyran ?	37.86	134	0.47
38	2-(3-chloroprop-1-enyloxy)ethan-1-ol	38.58	136	1.32
39	2-chloro-1-propanol	40.06	94	0.39
40	2-methyl-2-cyclopenten-1-one	40.64	96	0.35
41	1,1-dimethoxy-2-butyne	42.13	114	0.39
42	acetic acid	45.27	60	0.26
43	2-furancarboxyl chloride	45.82	130	0.21
44	4-(chloromethyl)-2-vinyl-1,3-dioxolane	47.32	148	1.23
45	1-(2-furanyl)ethanone	49.23	110	trace
46	2-(3-chloroprop-1-enyloxy)propanal ?	49.39	148	4.46
47	3-methyl-2,5-furandione	50.10	112	0.72
48	benzaldehyde	50.62	106	0.32
49	3-chloro-1-propanol	51.66	94	0.30
50	2-(3-chloro-2-hydroxypropoxy)propan-1-ol ?	53.45	168	2.42
51	3-chloro-1-(2-chloro-isopropoxy)prop-1-ene	55.08	169	0.56

TABLE 9.1.13 (continued). Compounds identified in the pyrogram of polyepichlorohydrin $M_w = 700,000$ as shown in Figure 9.1.18.

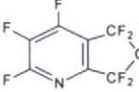
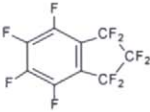
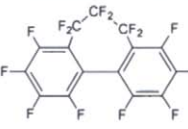
Peak	Compound	Ret Time	MW	Area %
52	unknown [43(100), 41(61), 77(56), 114(35), 107(33)]	56.24		1.79
53	unknown [84(100), 43(94), 93(63), 75(31), 58(29)]	60.65		0.57
54	unknown [43(100), 71(86), 41(79), 68(77), 147(38), 188(32)]	62.14		0.18
55	1,3-dichloro-1-propanol	63.69	128	1.75
56	2,3-dichloro-1-propanol	67.97	128	0.43
57	unknown [41(100), 119(37), 57(29), 58(27), 77(25), 79(22)]	70.49		6.63
58	unknown [41(100), 77(33), 84(24), 93(23), 119(13), 79(22)]	74.29		2.26
59	unknown [41(100), 175(44), 57(31), 55(28), 177(15), 119(15)]	83.22		2.60
60	unknown [101(100), 121(59), 45(51), 41(38), 149(41), 198(8)]	88.25		1.24
61	unknown [41(100), 75(46), 119(42), 77(37), 93(22), 203(3)]	92.83		4.13
62	unknown [93(100), 141(89), 75(78), 143(55), 171(32), 173(25)]	101.23		4.14
63	unknown [41(100), 93(60), 57(30), 121(29), 119(20), 189(2)]	106.77		8.83
64	unknown [41(100), 93(65), 121(32), 57(30), 119(21), 169(5)]	107.31		8.03
65	unknown [41(100), 55(33), 147(25), 57(20), 119(14)]	120.32		3.32

Polyepichlorohydrin pyrolysate is a complex mixture of compounds, somehow similar to that obtained by the pyrolysis of poly(ethylene oxide). The breaking of the C–O bonds is probably easier than that of C–C bonds. However, C–C bonds are more frequently cleaved in pyrolysis of polyepichlorohydrin than in that of poly(propylene oxide). The elimination of HCl (4.7% in the pyrogram) further complicates the pyrogram of this polymer.

A study on thermal degradation pyrolysis of polyepichlorohydrin (PECH) using only Py-MS [25] showed that PECH degrades via a random cleavage mechanism, mainly with the cleavage of C–O bonds, which are weaker than C–C bonds. In addition to backbone cleavage, polyepichlorohydrin also shows elimination of the side groups with evolution of HCl. Intramolecular crosslinking following the loss of side chains has been proposed as an explanation for the formation of fragments with cyclic end groups at the final stages of thermal decomposition of PECH.

Among other poly(halogenated ethers), poly(fluorinated ethers) are used as thermally and chemically stable oils, greases and elastomers, while certain poly(brominated ethers) are used as fire retardant epoxy resins [28]. A typical poly(fluorinated ether) is poly(hexafluoropropylene oxide), CAS# 60164-51-4, which has the formula $C_2F_5[-OCF_2CF(CF_3)-]_nF$. The end groups of the polymer may be different than -F or - C_2F_5 , depending on the polymer preparation. This polymer prepared with relatively low M_w can be used as a very high boiling point fluid with low viscosity. Some other polymers of practical interest include poly(oxy-methylene-hexafluoropropylene-methylene-oxy-methylene) or $-[O-CH_2-(CF_2)_3-CH_2-O-CH_2]_n-$ and similar polymers that contain in the backbone phenylene or other groups. Some results reported in literature regarding thermal properties of these polymers are indicated in Table 9.1.14.

TABLE 9.1.14. Summary regarding reports in literature on the thermal decomposition of several poly(fluorinated ethers) [13].

Polymer	Temp. °C	Results	Ref.
$-\text{[O-CH}_2(\text{CF}_2)_3\text{-CH}_2\text{-O-CH}_2\text{]}_n-$	510–540	$\text{CH}_3(\text{CF}_2)_3\text{CH}_2\text{OCH}_3$ (46.9%) relative areas of GC traces, $\text{CH}_3(\text{CF}_2)_3\text{CH}_3$ (14%), $\text{CH}_3\text{CF}_2\text{CF}_2\text{H}$ (6.7%), $\text{CF}_2=\text{CH}_2$ (6.7%), $\text{CF}_2\text{HCF}_2\text{H}$ (2.3%) HF (50%), $\text{CH}_3(\text{CF}_2)_3\text{H}$ (27.6%), $\text{CF}_2=\text{CH}_2$ (7.8%), $\text{CF}_2\text{HCF}_2\text{H}$ (4.3%),	52
$-\text{[O-CH}_2(\text{CF}_2)_3\text{-CH}_2\text{-O-}m\text{-C}_6\text{NF}_3\text{]}_n-$	510–540	 (5.6%), $\text{C}_5\text{NF}_3\text{H}_2$ (3.1%) $\text{CF}_2=\text{CH}_2$ (17.0%), $\text{CH}_3(\text{CF}_2)_3\text{H}$ (16.5%), $\text{CF}_2\text{HCF}_2\text{H}$ (6.4%),	52
$-\text{[O-CH}_2(\text{CF}_2)_3\text{-CH}_2\text{-O-}p\text{-C}_6\text{F}_4\text{]}_n-$	510–540	 (9.4%), $\text{CH}_3\text{CF}_2\text{CF}_2\text{H}$ (4.1%), $\text{C}_6\text{F}_5\text{H}$ (9.6%), $\text{C}_6\text{F}_5\text{CHO}$ (7.2%), $\text{C}_6\text{F}_4\text{HCHO}$ (4.9%), $\text{C}_6\text{F}_4\text{H}_2$ (3.3%) HF (31%), $\text{CF}_2=\text{CH}_2$ (22.0%), $\text{CH}_3(\text{CF}_2)_3\text{H}$ (19.7%), $\text{CF}_2\text{HCF}_2\text{H}$	52
$-\text{[OCH}_2(\text{CF}_2)_3\text{-CH}_2\text{-O-}p\text{-C}_6\text{F}_4\text{-}p\text{-C}_6\text{F}_4\text{]}_n-$	510–540	 (8.1%), (10.1%), $\text{C}_6\text{F}_5\text{C}_6\text{F}_4\text{H}$ (5.6%), $\text{C}_6\text{F}_4\text{HC}_6\text{F}_4\text{H}$ (9.3%)	52

The results for a Py-GC/MS analysis of a poly(hexafluoropropylene oxide) sample, CAS# 60164-51-4, are shown in Figure 9.1.19. The pyrolysis was done in similar conditions as for other examples previously discussed (see Table 4.2.2).

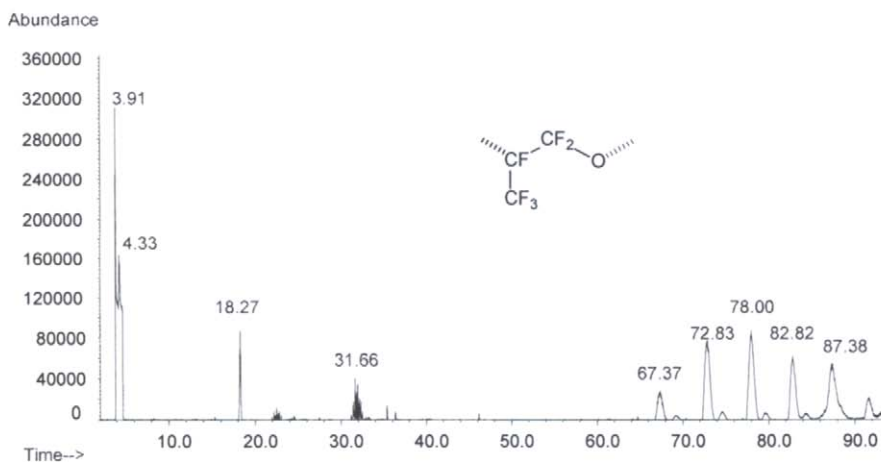


FIGURE 9.1.19. Result for a Py-GC/MS analysis of poly(hexafluoropropylene oxide). Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

As shown in Figure 9.1.19, the decomposition of the polymer at 600° C generates few volatile compounds (the abundance scale of the pyrogram is very low). The peaks at 3.91 min. and 4.33 min. correspond to the traces of air and carbon dioxide, respectively. The peak at 18.27 min. is water, adsorbed on the polymer. The mass spectra of the compounds eluting around 23 min. and also those eluting around 31 min. show very high molecular weight. Similarly to poly(propylene oxide), the carbon atoms for each monomer unit are asymmetric, and groups of diastereoisomers poorly separated appear in the pyrogram. Pyrolysis of the same polymer at 850° C maintaining the other conditions identical to the previous experiment is shown in Figure 9.1.20.

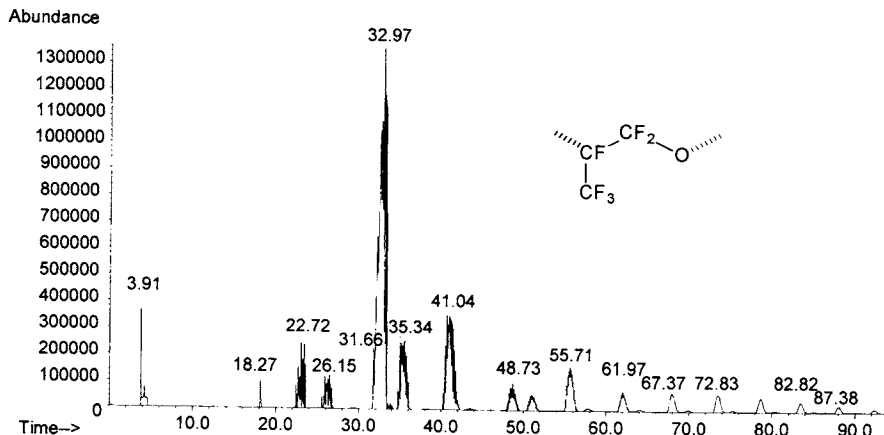


FIGURE 9.1.20. Result for a Py-GC/MS analysis of poly(hexafluoropropylene oxide). Pyrolysis done on 0.4 mg material at 850° C in He, with the separation on a Carbowax type column.

The pyrogram at 850° C shows significantly higher abundance of volatile compounds, but the separation is still very poor. Sixteen peaks eluting around 22.72 min. have identical spectra and correspond to a pentamer. The tentatively assigned formula for these compounds is $C_2F_5[-OCF_2CF(CF_3)]_5F$ with MW = 968. The spectrum for any of the peaks in the group is shown in Figure 9.1.21.

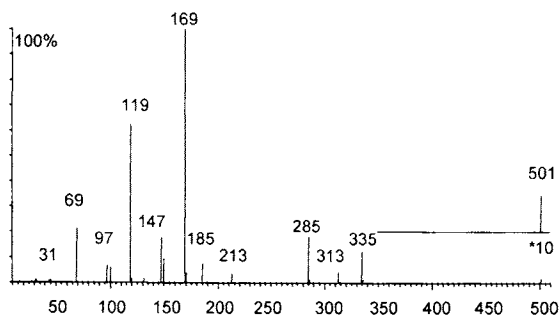


FIGURE 9.1.21. Mass spectrum of one of the 16 peaks eluting around 22.72 min. in the pyrogram shown in Figure 9.1.20. The tentatively assigned compounds to these spectra have the formula $C_2F_5[-OCF_2CF(CF_3)]_5F$ with MW = 968.

The peaks from the next group, eluting around 26.15 min., do not have identical spectra with those from the group eluting around 22.72 min. This indicates some structural differences since the mass spectrum of a hexamer should not be different from that of a pentamer. In addition to that, this next group eluting around 26.15 min. is also formed from 16 peaks with identical spectra, which shows that five asymmetric carbon atoms are present in these compounds. The tentative formula for the compounds generating the set of peaks eluting around 26.15 min. is $C_2F_3[-OCF_2CF(CF_3)]_5F$ with the MW = 930. The spectrum for any of the peaks in the group is shown in Figure 9.1.22.

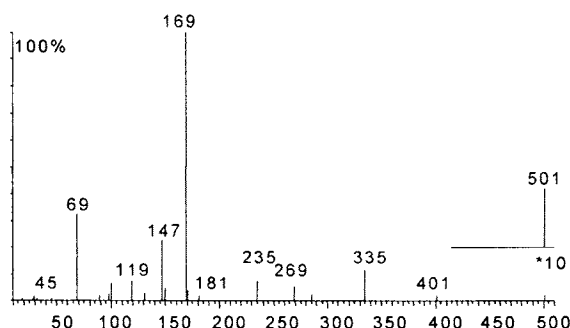


FIGURE 9.1.22. Mass spectrum of one of the 16 peaks eluting around 26.15 min. in the pyrogram shown in Figure 9.1.20. The tentatively assigned compounds to these spectra have the formula $C_2F_3[-OCF_2CF(CF_3)]_5F$ with MW = 930.

The peaks eluting around 32.97 min. have identical spectra with those eluting at 22.72 min., as expected for a hexamer. The number of peaks in this group is probably 32, but the separation was not achieved. The group of peaks eluting around 35.36 min. have identical spectra with those eluting around 26.15 min., and the formula tentatively assigned for this group is $C_2F_3[-OCF_2CF(CF_3)]_6F$. Fragments with an increasing number of monomeric units are generated in the pyrogram at higher retention times. This demonstrates that the pyrolysis at 600° C shows only very high M_w compounds.

Thermal decomposition of a fire retardant brominated epoxy resin containing 20% Br has been reported in literature [28]. The material was prepared by curing a mixture of diglycidyl ethers of bisphenol A, tetrabromobisphenol A, and 4,4'-diaminodiphenylsulphone. The thermal stability of this material has been studied by high-resolution thermogravimetry and IR spectroscopy. Programmed heating condition using inert atmosphere has been applied to collect gaseous and high boiling products, which have been identified by GC-MS. The resin generated from crosslinking of {2,2'-[(1-methylethylidene)-bis(2,6-dibromo-4-phenylene)oxymethylene]}bisoxirane was evaluated for thermal decomposition. The resin generated HBr upon heating around 400° C [53].

- Copolymers of other ethers

The ether groups are present in a number of copolymers. Some of these, involving poly(ethylene glycol) as comonomer were discussed previously (see Figure 9.1.9). Others are present in epoxy resins and also were discussed previously. Some macromolecules with ether groups in the backbone are *alt* copolymers and can be identified as unique compounds (like homopolymers) and are discussed separately (see Section 9.3. The remaining category includes copolymers where various ethers (different than ethylene glycol) are used as comonomers in copolymers. Examples of this type are poly(propylene oxide-co-allyl glycidyl ether), poly(propylene oxide-co-allyl glycidyl ether-co-epichlorohydrin), nylon 12-*block*-poly(tetramethylene glycol), etc. Several polymeric blends also contain polymers with ether groups, such as polystyrene/poly(phenylene oxide) blend that acts as a high impact polystyrene. Thermal decomposition of this blend (40 S/60 PPO) between 300° C and 360° C generates ethylbenzene, styrene, α -methylstyrene, 2-methylphenol, 2,6-dimethylphenol, 2,4-dimethylphenol, 2,4,6-trimethylphenol, 1,3-diphenylpropane, 2,4-diphenyl-1-butene, 2,4,6-triphenyl-1-hexene, and PPO dimers [54]. Various other copolymers with ether groups are also known and some were studied using pyrolytic techniques [55, 56]. Some of these are *alt*-copolymers and are discussed separately in Section 9.3. Others are more complex molecules and are discussed in connection with the copolymers of other polymer types (see e.g. Chapters 10 and 16).

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9.2 POLY(ACETALS)

- General aspects

Polyacetals form a different subclass of compounds with oxygen in the backbone chain. In this group are included polymers that contain the group $-O-C(R_2)-O-$ and can be formed from the polymerization of aldehydes or ketones. A typical example of a polymer from this class is paraformaldehyde or polyformaldehyde or polyoxymethylene $(CH_2O)_n$. Polyoxymethylene can be prepared by anionic catalysis from formaldehyde in an inert solvent. Acetylation of the $-OH$ end groups of the polymeric chain is common since it improves the thermal stability of the polymer. Some results reported in literature regarding thermal decomposition of these polymers are indicated in Table 9.2.1 [1].

TABLE 9.2.1. Summary regarding reports in literature on the thermal decomposition of several poly(acetals).

Polymer	Temp. °C	Results	Ref.
paraformaldehyde	room temp.	distribution of oligomers measured by pyrolysis	2
poly(acetaldehyde)		acetaldehyde	3
poly(oxymethylene)		100% monomer	4
poly(oxymethylene)	100–180	100% formaldehyde; inverse relationship between molecular weight and rate for hydroxyl terminated polymers; acetylation of terminal hydroxy groups inhibits the reaction	5
poly(oxymethylene)	unspecified	formaldehyde formed by chain unzipping; the modified end-groups improve thermal stability	3
poly(oxymethylene-oxyethylene)	314–338	major volatile products CH ₄ , C ₂ H ₆ , C ₂ H ₄ , C ₂ H ₂ , HCO ₂ C ₂ H ₅	6
poly(oxytrichloromethyl methylene) or poly(trichloroacetaldehyde)	ambient (in time)	monomer	7

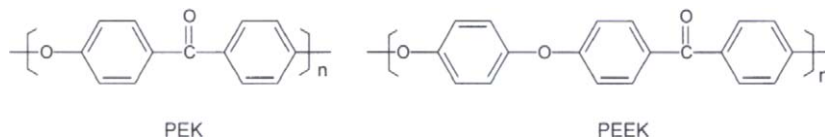
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9.3 POLY(ETHER-ALT-KETONES) AND OTHER POLYMERS CONTAINING ETHER-ALT GROUPS

- Poly(ether-alt-ketones)

Ether groups are present in polymers containing other functionalities in the backbone. Among these are the *alt*-polymers poly(oxy-1,4-phenylene-carbonyl-1,4-phenylene) or poly(aryl ether ketone) or poly(ether ketone) or PEK, poly(aryl ether ether ketone) or PEEK, poly(aryl ether ketone ketone) or PEKK, poly(aryl ether ketone ether ketone ketone) or PEKEKK, etc. The structures of PEK and PEEK are shown below:



The polymers from this class are typically obtained from a polycondensation reaction. For example, PEEK can be obtained from hydroquinone and 4,4'-difluorobenzophenone in the presence of potassium carbonate. Other synthesis paths are known such as electrophilic condensations in the presence of Friedel-Crafts catalysts.

The polymers have good thermal and mechanical properties. For example, PEK shows only about 5% weight loss when heated in N₂ at 520° C [1, 2].

Thermal decomposition of the polymer generates fragments of the polymeric chain and dibenzofuran derivatives. At higher temperatures CO, CO₂ and aromatic hydrocarbons are formed. In the presence of potassium carbonate and heating around 340° C, PEKEKK undergoes transesterification reactions forming polymers with ether-ketone ether-ketone-ketone sections. Some results reported in literature regarding thermal properties of these polymers are indicated in Table 9.3.11.

TABLE 9.3.1. Summary regarding reports in literature on the thermal decomposition of PEK and PEEK [4].

Polymer	Temp. °C	Results	Ref.
poly(oxy-1,3-phenylene-carbonyl-1,4-phenylene) or poly(ether ketone) or mPEK	420	CO, CO ₂ , hydrocarbons	2
poly(oxy-1,4-phenylene-carbonyl-1,4-phenylene) or poly(ether ketone) or PEK	390, 490, 530	low MW polymer at 490° C produces benzene, phenol, benzaldehyde, 4-hydroxybenzaldehyde, diphenyl ether, biphenylene, benzophenone, series of -H, -OH and -CHO terminated chain fragments containing less than eight aromatic units and fragments containing dibenzofuran units. High MW polymer at 530° C as above. Low MW polymer at 390° C produces significant quantities of 4-hydroxybenzaldehyde and benzophenone-4,4'-diol	3
poly(oxy-1,4-phenylene-carbonyl-1,4-phenylene) or poly(ether ketone) or PEK	506	phenol, dibenzofuran, benzofuran derivatives, mixtures of oligomers mostly hydroxy terminated	5
poly(oxy-1,4-phenylene-oxy-1,4-phenylene-carbonyl-1,4-phenylene) or poly(ether ether ketone) or PEEK	506	phenol, dibenzofuran, benzofuran derivatives, mixtures of oligomers mostly hydroxy terminated	5
poly(oxy-1,4-phenylene-oxy-1,4-phenylene-carbonyl-1,4-phenylene) or poly(ether ether ketone) or PEEK	750, 800, 850, 900, 980	C ₄ diene, C ₅ diene, benzene, toluene, benzoquinone, phenol, naphthalene, diphenyl, diphenyl ether, dibenzofuran, diphenyl ketone, 4-hydroxy diphenyl, 3-hydroxy diphenyl, 4-penoxy phenol, dibenzo-1,4-dioxan, 4-hydroxydiphenyl ketone, 1,4-diphenoxybenzene	6
sulfonated poly(ether ether ketone) or sulfonated PEEK	750, 800, 850, 900, 980	SO ₂ , C ₄ diene, C ₅ diene, benzene, toluene, benzoquinone, phenol, naphthalene, diphenyl, diphenyl ether, dibenzofuran, diphenyl ketone, 4-hydroxy diphenyl, 3-hydroxy diphenyl, 4-penoxy phenol, dibenzo-1,4-dioxan, 4-hydroxydiphenyl ketone, 1,4-diphenoxybenzene	6

Pyrolysis studies on PEEK by thermogravimetry/MS and Py-GC/MS were reported in literature [7]. The compounds described to be generated in the Py-GC/MS experiment, which was performed at 971° C, are shown in Table 9.3.2.

TABLE 9.3.2. *Compounds identified in the pyrogram of PEEK [7].*

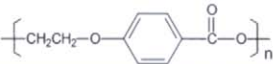
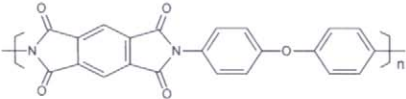
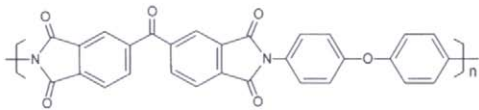
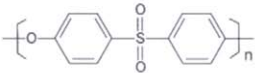
Peak	Compound	MW	Peak size*
1	benzene	78	L
2	phenol	94	L
3	naphthalene	128	M
4	hydroquinone	110	M
5	biphenyl	154	M
6	diphenyl ether	170	M
7	dibenzofuran	168	M
8	benzophenone	182	M
9	4-phenylphenol	170	S
10	4-phenoxyphenol	186	S
11	2-dibenzofuranol	184	S
12	hydroxybenzophenone	198	S
13	diphenoxybenzene	262	S
14	bis(phenoxy)benzophenone	355	S

The study indicated that the random chain scission occurs primarily at the ether linkage, and only under more severe pyrolysis conditions does it involve the ketone linkage.

- Other *alt*-copolymers containing ether groups in the backbone

The ether group is common in some other *alt*-copolymers. Many of these compounds have practical applications. For example, poly(ethylene oxybenzoate) is used as a filament yarn in the silk clothing industry. Other polymers are used as epoxy resins. Several examples of such ether-*alt*-different groups are given in Table 9.3.3. Pyrolysis of these macromolecules generates compounds indicative of their composition. However, the cleavage of C_{aromatic}-O bond occurs with more difficulty compared to C_{aliphatic}-O bond, and the resulting fragments may be more difficult to assign in the case of an unknown polymer. Non-alternating copolymers with a high enough proportion of comonomer may generate for these compounds rather similar pyrograms as the *alt*-copolymer. For example, thermal decomposition of poly(ether ketone-co-ether sulfone) with comonomer ratios 1/3, 3/1, 1/1 mol/mol (random) and 1/1 (*alt*) have the same decomposition products with distribution varying with composition. These compounds are biphenyl, hydroquinone, 4-phenoxyphenol, benzaldehyde, 4-hydroxybenzaldehyde, diphenyl sulfone, diphenylether, phenol, benzophenone-4,4'-diol, and two series of chain fragments containing PEK and PES units with -H, -OH and -CHO ends [3].

TABLE 9.3.3. Examples of *alt*-copolymers containing ether groups and other groups in the backbone.

Type	Name	Structure
ether- <i>alt</i> -ester	poly(ethylene oxybenzoate)	
ether- <i>alt</i> -pyromellitimide	poly[pyromellitic dianhydride- <i>alt</i> -bis(4-aminophenyl)ether]	
bis(4-aminophenyl)ether- <i>alt</i> -3,3',4,4'-benzophenonetetracarboxylic dianhydride	poly(3,3',4,4'-benzophenonetetracarboxylic dianhydride- <i>alt</i> -4,4'-oxydianiline)	
ether-sulfone	poly(oxy-1,4-phenylenesulfonyl-1,4-phenylene)	

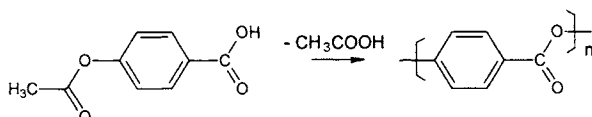
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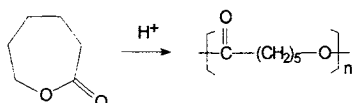
CHAPTER 10

*Polymers Containing Ester Groups in the Backbone***10.1 POLY(ESTERS)****- General aspects**

Poly(esters) are common polymers used as both thermoplastic materials and as fibers. The polymeric chain contains an acid fragment and an alcohol fragment. Similarly to polyamides, two series of polyesters are known, one resulting from a hydroxy acid or a lactone, having the general structure $[-O-R-C(O)-]_n$, and the other resulting from a diacid and a diol (or polyol) with the general formula $[-O-R^a-O-C(O)-R^b-C(O)-]_n$. For example, of the first type is poly(*p*-oxybenzoyl) or poly(4-hydroxybenzoic acid), CAS# 30729-36-3, which can be viewed as generated from self condensation of 4-hydroxybenzoic acid. In practice, the synthesis is done using *p*-acetoxybenzoic acid by elimination of the acetic acid at 250° C as shown below:

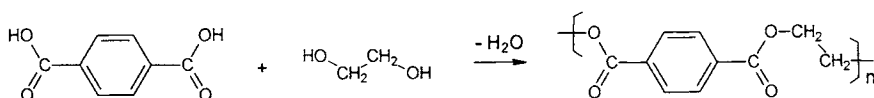


Many poly(esters) where the acid group and hydroxy group originate from the same molecule can be obtained from lactones using an acid catalyzed ring opening as shown below for a hexalactone (caprolactone):



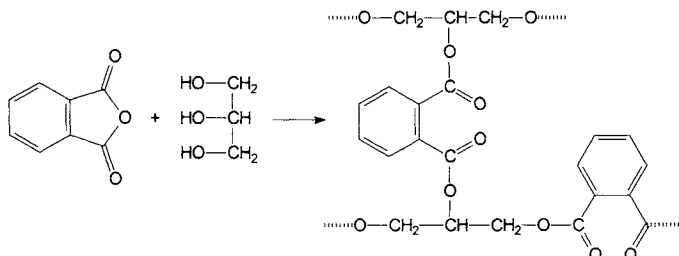
When the polyester is formed by a condensation reaction with water elimination, the hydrocarbon segment of the backbone can be aliphatic or aromatic, the -COOH and the -OH groups being connected either to an aliphatic segment or to an aromatic ring.

To the diacid and diol type polyester belongs, for example, poly(ethylene terephthalate), CAS# 25038-59-9, which can be viewed (and synthesized) from terephthalic acid and ethylene glycol by water elimination, as shown below:



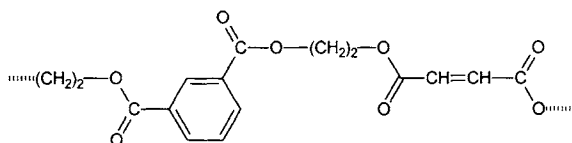
Other procedures to obtain the polymer include the use of terephthalic acid esterified to its dimethyl ester, which by a transesterification reaction with ethylene glycol generates the polymer. In addition to ethyleneglycol, other diols can be used in the esterification reaction, such as 1,4-butanediol, 1,4-cyclohexanedimethanol, 1,6-hexanediol, etc.

Some polyesters have a crosslinked structure when a polyfunctional alcohol or acid is used for the synthesis. For example, phthalic anhydride and glycerol form crosslinked polymers known as alkyds (name derived from alcohol and acids). The reaction is shown schematically below:



Alkyd resins have applications as surface coating materials, and they can be mixed with unsaturated fatty acids or triglycerides of unsaturated acids having the capability to cure by oxidation.

A different type of crosslinking is possible for esters with the diacids (or diols) containing double bonds in the molecule. This is more common for ester copolymers. For example, an isophthalic acid/fumaric acid/ethylene glycol polyester has the structure shown below:



Other acids can replace the isophthalic acid, such as orthophthalic acid, or the diol, such as bisphenol A. Also, other unsaturated diacids can be used instead of fumaric acid, such as chlorendic acid, which is 1,4,5,6,7,7-hexachlorobicyclo[2.2.1]-5-heptene-2,3-dicarboxylic acid, CAS# 115-28-6. The resulting ester has the capability to participate in copolymers, for example with styrene by the opening of the double bond. A crosslinked molecule results from this process, known as a thermoset.

- Polyesters with aliphatic and cycloaliphatic backbone

A number of polyesters with aliphatic or cycloaliphatic backbone are used in practice. Among these are polylactic acid, poly(hydroxyacetic acid), poly-caprolactone, poly(ethylene glycol succinate), poly(ethylene glycol adipate) CAS# 24938-37-2, poly(1,2-ethandiol nonanedioic acid ester) CAS# 26760-99-6, poly(1,4-butylene glycol adipate) CAS# 25103-87-1, poly(1,10-decanediol adipate) CAS# 28552-31-0, poly(1,10-decanediol sebacate) CAS# 27514-86-9, poly(3-hydroxy-2,2-dimethylpropanoic acid) CAS# 30622-81-2, poly(3-hydroxybutyrate) CAS# 26063-00-3, etc. Some of the polymers obtained from aliphatic acids and aliphatic hydroxy components are biodegradable [1] and have various medical applications for surgical sutures and drug delivery systems. Others are used for packaging, films, stationary phases in chromatography, etc. Pyrolysis and pyrolysis applications of various polyesters are

described frequently in literature [2–11]. The decomposition products reported in literature for some polyesters containing an aliphatic acid and an aliphatic alcohol, when heated in an inert atmosphere are indicated in Table 10.1.1 [12].

TABLE 10.1.1. Summary regarding literature information on thermal decomposition of several aliphatic polyesters [12].

Polymer	Temp. °C	Results	Ref.
poly((D)-oxy-1-oxotetramethylene) or poly(4-hydroxy-butylate)	320	cyclic oligomers (γ -butyrolactone and higher homologues)	13
poly(lactide)	365	H ₂ O, CO ₂ , etc.	14
poly(oxy-1-oxo-2,2-dimethyltri-methylene) or poly(α,α -dimethyl- β -propiolactone)	250–600	isobutylene and CO ₂	15
poly(oxy-1-oxo-2,2-trimethylene) or poly(β -propiolactone)	180–220	acrylic acid	16
poly(oxy-1-oxo-2-methylene) or poly(L-lactic acid)	500	CO, CO ₂ , acetaldehyde, acetone, acrylic acid, acetic acid, DL-lactide, <i>meso</i> -lactide, cyclic oligomers up to nonamer, 2,3-pentanedione, lactoyl lactic acid	17
poly(oxy-1-oxohexamethylene)	220	monomer (ϵ -caprolactone)	18
poly(oxycarbonyl-3-pentylidene)	200–500	<i>cis</i> - and <i>trans</i> -2-ethyl crotonic acid (major products)	19
poly(oxycarbonyl-cyclohexylidene)	200–500	cyclohexen-1-carboxylic acid, cyclohexanone	20
poly(oxycarbonyl-cyclopentylidene)	200–500	cyclopenten-1-carboxylic acid, cyclopentanone, dicyclopentyl glycolide	20
poly(oxyethyleneoxy-adipoyl)	ambient to 500	cyclic oligomers, CO, CO ₂ , acetaldehyde, 2-ethylacrolein	21
poly(oxytetramethylene-oxysebacoyl)	ambient to 500	CO ₂ , H ₂ O, butadiene, tetrahydrofuran	22
poly(tetramethylene succinate)	550	1,3-butadiene, ethylene, CO ₂ , H ₂ O, 3-buten-1-ol, 2-oxetanone, cyclopropanone, succinic anhydride, succinic acid monoethyl ester, succinic acid monobutyl ester, succinic acid monobutenyl ester, ethyl butenyl succinate, ethenyl butenyl succinate, ethyl butenyl succinate, butyl butenyl succinate	23
poly((D)-oxy-1-oxo-3-methyl-trimethylene) or poly(3-hydroxybutyrate)	ambient to 338	dimer (41.2 wt.%), crotonic acid (35.3), trimer (12.5), tetramer (2.9), isocrotonic acid (0.9). Small amounts of CO ₂ , propene, ketene, acetaldehyde, and β -butyrolactone are formed at higher temperatures due to decomposition of primary products	24
poly((D)-oxy-1-oxo-3-methyl-trimethylene) or poly(3-hydroxybutyrate)	250	crotonic acid (64.4% of original polymer), dehydrated dimer (7.2%), dehydrated trimer (1.2%)	25
Poly((D)-oxy-1-oxo-3-methyl-trimethylene) or poly(3-hydroxybutyrate)	400	crotonic acid (65.4% of original polymer), dehydrated dimer (8.2%), dehydrated trimer (2.1%)	25
Poly((D)-oxy-1-oxo-3-methyl-trimethylene) or poly(3-hydroxybutyrate)	600	crotonic acid (58.3% of original polymer), dehydrated dimer (9.0%), dehydrated trimer (2.7%)	25
poly((D)-oxy-1-oxo-3-methyl-trimethylene) or poly(3-hydroxybutyrate)	350	crotonic acid (<i>trans</i>), dehydrated dimer (<i>trans</i>), dehydrated trimer and tetramer (<i>cis/trans</i> not resolved)	26

Poly(lactic acid), poly(L-lactide) or poly(oxy-1-oxo-2-methylene) is available in atactic form, CAS# 33135-50-1, and both syndiotactic form (CAS# 85114-66-5) and isotactic form (CAS# 85066-50-8). The results for a Py-GC/MS analysis of a poly(L-lactide) sample (atactic) with $M_w = 10,000\text{--}150,000$ are shown in Figure 10.1.1. The polymer has the idealized formula $[-OCH(CH_3)CO-]_n$. The pyrolysis was done at 600°C in He at a heating rate of 20°C/ms with 10 s THT. The separation was done on a Carbowax column (60 m, 0.32 mm i.d., 0.32 μm film thickness) with the GC starting at 40°C with a ramp of 2°C/min. up to 240°C and a final oven time of 20 min. (see Table 4.2.2). The MS was operated in EI+ mode. The peak identification for the chromatogram shown in Figure 10.1.1 was done using MS spectral library searches only and is given in Table 10.1.2.

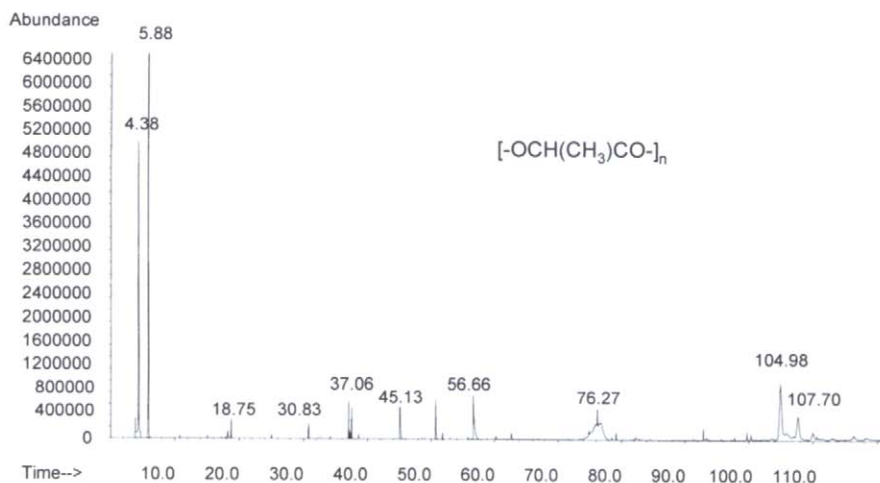


FIGURE 10.1.1. Pyrogram from a Py-GC/MS analysis of a poly(L-lactide) sample with $M_w = 10,000\text{--}150,000$. Pyrolysis done on 0.4 mg material at 600°C in He, with the separation on a Carbowax type column.

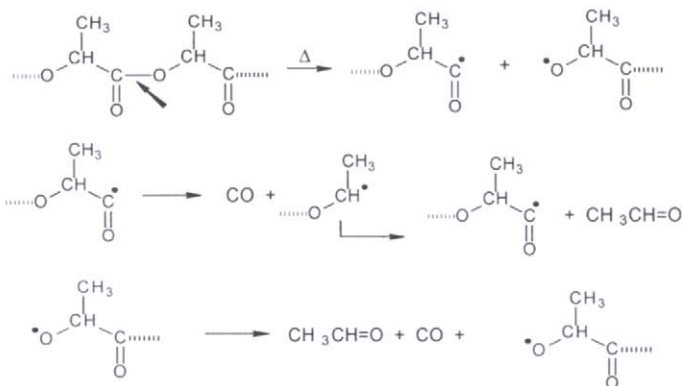
TABLE 10.1.2. Compounds identified in the pyrogram of a poly(L-lactide) sample with $M_w = 10,000\text{--}150,000$ as shown in Figure 10.1.1.

Peak	Compound	Ret. Time	MW	Area %
1	carbon monoxide	4.38	28	22.92
2	acetaldehyde	5.88	44	40.41
3	propanal	7.40	58	trace
4	propanone	8.03	58	trace
5	2-butanone	10.76	72	trace
6	ethanol	12.33	46	trace
7	2-butenone	12.78	70	trace
8	propanoic acid ethyl ester	13.23	102	trace
9	2,3-butandione	14.14	86	trace
10	2-propenoic acid ethyl ester	15.09	100	trace
11	2-ethyl-5-methylfuran	17.21	110	trace
12	2-butenal + traces of toluene	17.84	70	trace

TABLE 10.1.2 (continued). Compounds identified in the pyrogram of a poly(L-lactide) sample with $M_w = 10,000$ –150,000 as shown in Figure 10.1.1.

Peak	Compound	Ret. Time	MW	Area %
13	water	18.25	18	trace
14	2,3-pentandione	18.75	100	0.88
15	2-vinyl-5-methylfuran	25.05	108	trace
16	1-dodecene (impurity)	30.83	168	0.65
17	2-oxopropionic acid ethyl ester	32.79	116	trace
18	3-hexanone ?	34.22	100	trace
19	2,4,5-trimethyl-1,3-dioxolane	37.06	116	1.78
20	3-ethyl-2-hydroxy-2-cyclopenten-1-one ?	37.36	126	trace
21	2-ethyl-4-methyl-1,3-dioxolane	37.56	116	1.32
22	2-hydroxypropanoic acid ethyl ester	38.02	118	trace
23	5-methyl-2(3H)-furanone	44.36	98	trace
24	acetic acid	45.13	60	2.03
25	1-(acetyloxy)-2-propanone	45.86	116	trace
26	propanoic acid	50.73	74	2.57
27	propanoyloxyethylprop-2-enoate	51.83	172	trace
28	5-methyl-dihydro-2-(3H)-furanone	55.82	100	trace
29	2-propenoic acid	56.66	72	5.81
30	2-methyl-2-propenoic acid	60.23	86	trace
31	2,4-dimethyl-2,5-furandione	62.66	126	trace
32	4-pentenoic acid	66.86	100	trace
33	2-methyl-2-oxopentanoic acid ethyl ester	76.04	158	1.40
34	2,3-dihydro-4-hydroxy-2,5-dimethyl-3-furanone	78.52	128	trace
35	2-dodecanol (impurity)	99.90	186	trace
36	unknown [114(100), 222(74), 166(64), 180(61),...280(8)]	104.98		14.31
37	unknown [114(100), 210(58), 101(44), 168(46),...268(11)]	107.71		5.92

As shown in the pyrogram of poly(L-lactide), the main pyrolysis products are CO and acetaldehyde. The pyrolysis probably takes place by a free radical mechanism including the following reactions:



Rather different results during pyrolysis are obtained when the alkyl chain is longer, such as in the case of polycaprolactone. The results for a Py-GC/MS analysis of a polycaprolactone sample with $M_w = 14,000$ are shown in Figure 10.1.2. The polymer has the idealized formula $[-\text{O}(\text{CH}_2)_5\text{CO-}]_n$ and CAS# 24980-41-4. The pyrolysis was

done at 600° C in He at a heating rate of 20° C/ms with 10 s THT. The separation was done on a Carbowax column (60 m, 0.32 mm i.d., 0.32 µm film thickness) with the GC starting at 40° C with a ramp of 2° C/min. up to 240° C and a final oven time of 20 min. The MS was operated in EI+ mode. The peak identification for the chromatogram shown in Figure 10.1.2 was done using MS spectral library searches and is given in Table 10.1.3.

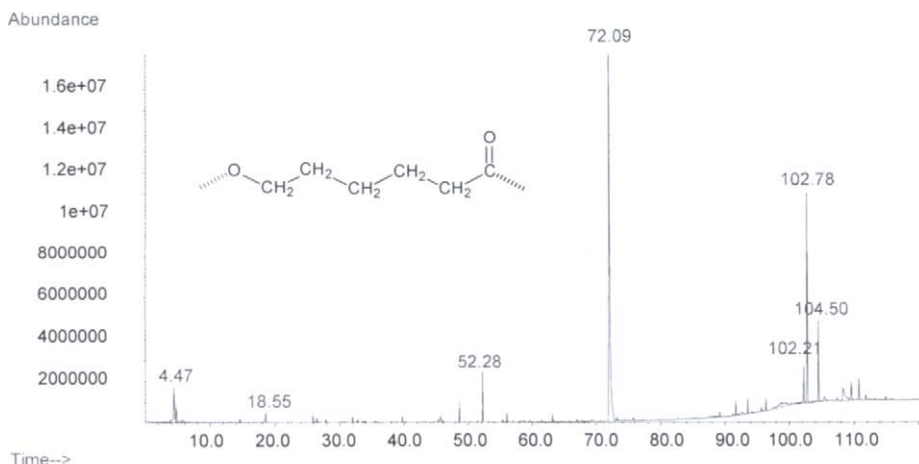


FIGURE 10.1.2. Pyrogram from a Py-GC/MS analysis of a polycaprolactone sample with $M_w = 14,000$. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

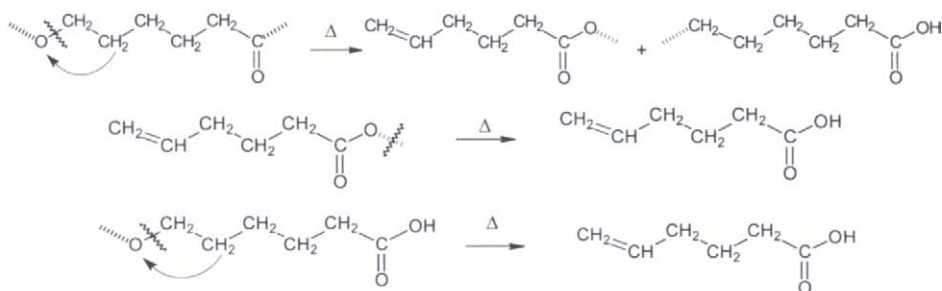
TABLE 10.1.3. Compounds identified in the pyrogram of a polycaprolactone sample with $M_w = 14,000$ as shown in Figure 10.1.2.

Peak	Compound	Ret. Time	MW	Area %
1	carbon dioxide	4.47	44	4.75
2	1-pentene	4.84	70	1.65
3	cyclopentene	5.75	68	trace
4	1,5-hexadiene	5.89	82	trace
5	pentanal	14.60	86	0.28
6	water	18.55	18	0.95
7	furfural	25.88	96	0.43
8	cyclopentanone	27.87	84	trace
9	1-cyclopropyl-2-propen-1-one	32.80	96	0.26
10	unknown [97(100), 114(66), 68(66), 60(65), 69(62)]	39.77	114	0.43
11	2-cyclohexen-1-one	45.35	96	trace
12	acetic acid	45.70	60	trace
13	3-ethyl-2,5-dimethyl-3-hexene ?	48.66	126	1.18
14	2-methyl-2-pentenoic acid	52.28	114	3.09
15	3-hexenoic acid ethyl ester	55.36	142	trace
16	1-methyl-2-cyclohexen-1-ol	56.08	112	0.50
17	pentanoic acid	59.70	102	trace
18	unknown [99(100), 86(75), 41(58), 69(52), 141(40), 140(30)]	63.18		0.56
19	5-hexenoic acid	72.09	114	52.03

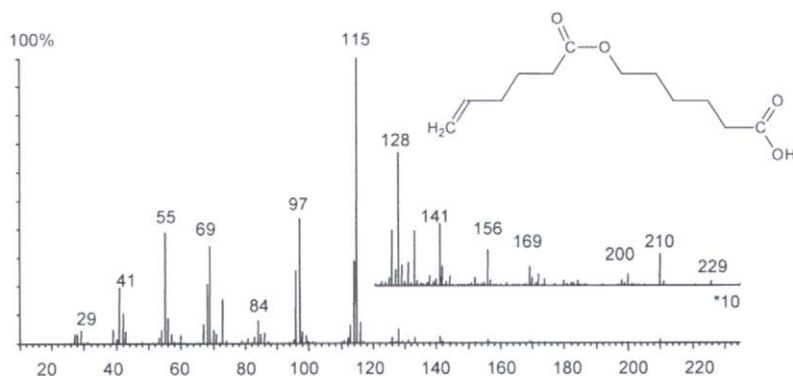
TABLE 10.1.3 (continued). Compounds identified in the pyrogram of a polycaprolactone sample with $M_w = 14,000$ as shown in Figure 10.1.2.

Peak	Compound	Ret. Time	MW	Area %
20	4-hexenoic acid	73.26	114	0.57
21	cyclopentanecarboxylic acid	75.70	114	trace
22	formic acid methylpropyl ester ?	91.66		trace
23	4-methyl-5-propyl-2H-furan-2-one ?	93.57	140	1.08
24	6-hexanoylhexanoic acid ?	102.21	230	3.33
25	6-hex-5-enoyloxyhexanoic acid	102.78	228	17.01
26	6-(6-oxohexanoyloxy)hexanoic acid ?	104.50	244	6.03
27	6-hydroxyhexanoic acid	108.30	132	3.56
28	2-(3-buten-1-yl)-cycloheptanone ?	109.56	166	2.05

For poly(caprolactone) the main reaction during pyrolysis is the formation of 5-hexenoic acid by a reaction as shown below:



The other components in the pyrolysate include fragments resulting from two units of 6-hydroxyhexanoic acid. One such component responsible for about 17% of the analyzed portion of the pyrolysate with the mass spectrum shown in Figure 10.1.3 was tentatively assigned as 6-hex-5-enoyloxyhexanoic acid.

FIGURE 10.1.3. Mass spectrum tentatively assigned to 6-hex-5-enoyloxyhexanoic acid ($MW = 228$).

More complicated pyrolysis process occurs for poly[di(ethylene glycol) adipate]. This polymer contains two types of C–O bonds that can be cleaved by pyrolysis. The results for a Py-GC/MS analysis of a poly[di(ethylene glycol) adipate] sample are shown in Figure 10.1.4. The polymer has CAS# 9010-98-3 and the idealized formula $[-OCH_2CH_2OCH_2CH_2O_2C(CH_2)_4CO-]_n$. The pyrolysis, separation, and peak identification were done similarly to the other examples previously discussed (see Table 4.2.2). The results of peak identification are given in Table 10.1.4.

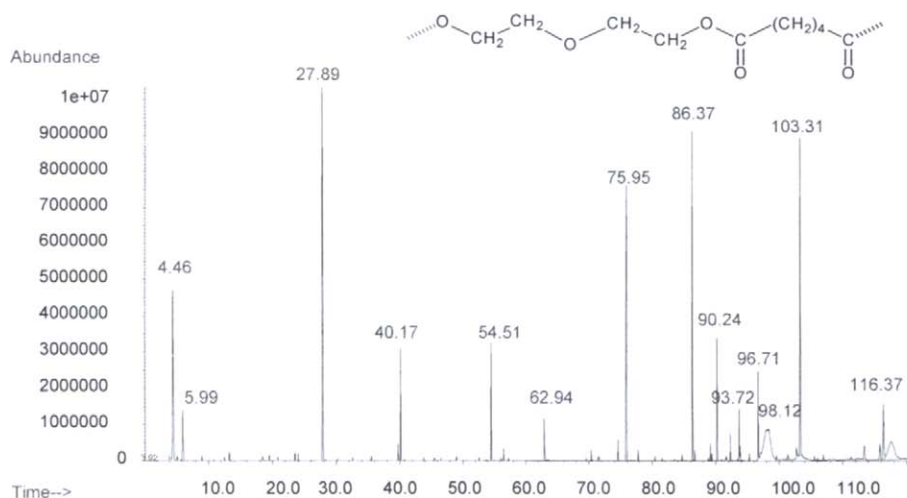


FIGURE 10.1.4. Pyrogram from a Py-GC/MS analysis of a poly[di(ethylene glycol) adipate] sample. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 10.1.4. Compounds identified in the pyrogram of a poly[di(ethylene glycol) adipate] sample shown in Figure 10.1.4.

Peak	Compound	Ret. Time	MW	Area%
1	carbon dioxide	4.46	44	9.51
2	formaldehyde	5.14	30	0.29
3	acetaldehyde	5.99	44	1.87
4	vinyl ether	6.01	70	0.76
5	2-propenal	8.99	56	0.23
6	ethanol	12.51	46	0.34
7	2-methyl-1,3-dioxolane	13.26	88	0.67
8	propanoic acid ethenyl ester	13.47	100	trace
9	2-propenoic acid ethyl ester	15.25	100	trace
10	water	18.45	18	0.25
11	2-butenic acid methyl ester	18.71	100	trace
12	2,5-dihydrofuran	18.92	70	trace
13	1,4-dioxane	19.49	88	0.35
14	hexanal	20.57	88	trace
15	pentanoic acid methyl ester	20.86	116	0.29
16	3-butenic acid ethyl ester	21.60	114	trace

TABLE 10.1.4 (continued). Compounds identified in the pyrogram of a poly[di(ethylene glycol) adipate] sample shown in Figure 10.1.4.

Peak	Compound	Ret. Time	MW	Area%
17	2-oxohexanoic acid methyl ester	23.54	144	0.31
18	pentanoic acid ethyl ester	24.03	140	0.34
19	1,1'-[1,2-ethanediylbis(oxy)]bis-ethene	26.64	114	trace
20	cyclopentanone	27.89	84	15.75
21	2-methylcyclopentanone	28.34	98	trace
22	2-ethoxyethanol	30.21	90	0.21
23	styrene	32.60	104	0.14
24	cyclohexanone	35.43	98	trace
25	2-methyl-2-cyclopent-1-one	35.60	96	0.29
26	2-cyclopent-1-one	39.78	82	0.69
27	2,2'-oxybis-ethanol diacetate	39.88	190	trace
28	2-(ethenyloxy)-ethanol	40.17	88	3.49
29	2,2'-oxybis-ethanol dipropionate	43.85	218	0.16
30	acetic acid	45.53	60	0.38
31	2,3-dimethyl-2-cyclopentene-1-one	45.94	110	trace
32	2-(2-prop-2-enoyloxyethoxy)ethyl prop-2-enoate	46.52	214	0.11
33	2,3-dimethyl-2-cyclopentene-1-one isomer	49.04	110	0.16
34	2-(2-prop-2-enoyl-oxyethoxy)ethyl but-3-enoate ?	52.58	228	0.14
35	2-(2-butanoyl-oxyethoxy)ethyl but-3-enoate ? or 2-(2-pentanoyloxyethoxy)ethyl prop-2-enoate ?	54.51	244	3.39
36	2-acetylcyclopentanone ?	56.08	126	0.30
37	1,2-ethandiol	56.49	62	0.60
38	unknown [69(100), 113(75), 41(27), 42(18), 126(2)]	57.26		0.24
39	2-[2-(ethenyloxy)ethoxy]-ethanol	62.77	132	trace
40	butanoic acid	62.94	88	1.91
41	hexandioic acid ethyl methyl ester	69.57	188	0.25
42	butanoic acid 3-methyl-2-methylpropyl ester ?	70.38	158	0.68
43	unknown [111(100), 157(48), 55(43), 83(27), 101(16)]	71.45		trace
44	1-cyclohexene-1-carboxylic acid ?	71.56	154	0.49
45	1,1-diethoxyethane ?	74.61	118	1.03
46	2,2'-oxybisethanol	75.95	106	14.14
47	ethane-1,1-diol dipropionate ?	77.79	174	0.60
48	diethyleneglycol monoacrylate	80.47	160	0.34
49	unknown [85(100), 57(61), 45(64), 129(48), 160(12)]	86.37		11.05
50	2-methyl-1,3-dioxolane-2-propanal	86.75	144	0.46
51	3-hydroxy-4-methylbenzaldehyde ?	90.24	136	4.09
52	unknown [187(100), 111(66), 73(56), 55(48), 155(37)]	92.32		0.99
53	unknown [201(100), 111(76), 73(65), 55(47), 155(47)]	93.72		2.51
54	unknown [129(100), 85(39), 57(23), 41(6), 190(1)]	96.71		2.81
55	unknown [240(100), 117(75), 91(70), 68(47), 31(37)]	98.12		2.50
56	5-[(2-hydroxyethyl)oxycarbonyl]pentanoic acid or adipic acid ethylene glycol monoester ?	103.31	190	10.30
57	unknown [175(100), 176(50), 55(10), 111(8)]	113.37		0.84
58	dihydro-3-phenylmethyl)-2(3H)-furanone ?	115.81	176	0.90
59	unknown [73(100), 155(92), 55(77), 99(66), 243(52), 111(42)]	116.37		2.88

The identification for the pyrolysate components of poly[di(ethylene glycol) adipate], as shown in Table 10.1.4, is tentative for many peaks. Only by using the similarity with certain spectra found in mass spectral libraries was it possible to make some of the tentative assignments. For example, the spectrum of 2-propenoic acid oxybis(1,2-ethanedioxy-1,2-ethnediyl) ester or tetraethyleneglycol dipropenoate is available in

NIST 98 mass spectral library (the compound is not found or expected in the pyrolysate). Based on the similarity with this spectrum, it was possible to tentatively assign some other spectra from the pyrogram to compounds such as 2-(2-prop-2-enoyloxyethoxy)ethyl prop-2-enoate (diethyleneglycol dipropenoate), 2-(2-prop-2-enoyloxyethoxy)ethyl but-3-enoate, 2-(2-butanoyloxyethoxy)ethyl but-3-enoate or 2-(2-pentanoyloxyethoxy)ethyl prop-2-enoate, etc. The library spectrum of tetraethyleneglycol dipropenoate, and the tentatively assigned spectra of 2-(2-prop-2-enoyloxyethoxy)ethyl prop-2-enoate and of 2-(2-prop-2-enoyloxyethoxy)ethyl but-3-enoate are shown in Figure 10.1.5.

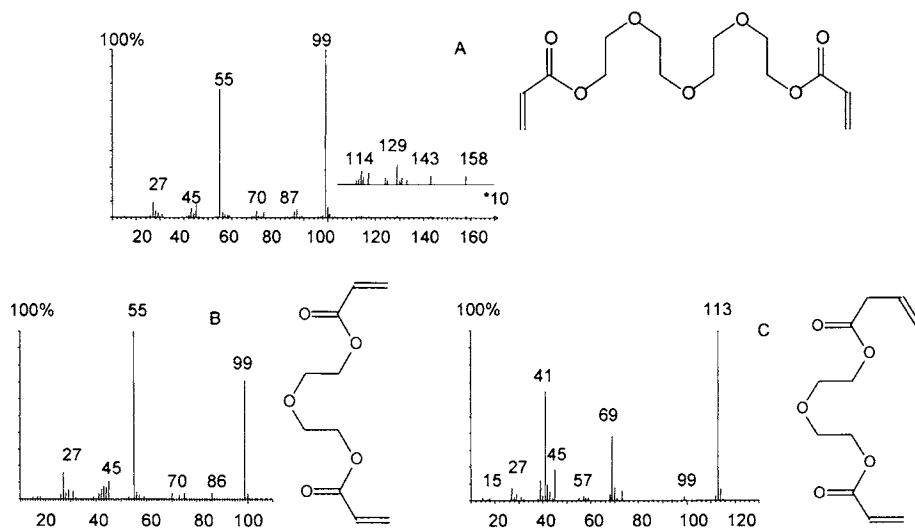
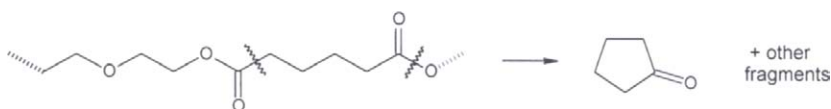


FIGURE 10.1.5. Mass spectra of tetraethyleneglycol dipropenoate MW = 302 (A) (from mass spectral libraries) and tentatively assigned spectra of 2-(2-prop-2-enoyloxyethoxy)ethyl prop-2-enoate MW = 214 (B) and 2-(2-prop-2-enoyloxyethoxy)ethyl but-3-enoate MW = 228 (C).

Although some of the peaks in the pyrolysate of poly[di(ethylene glycol) adipate] were not identified or only tentatively identified, it can be concluded that this polymer forms during pyrolysis fragments from both the diacid component and the diol. Since the diol contains itself a C—O—C group, it can further generate fragments as formed from the pyrolysis of diethylene glycol. Among these fragments are ethanol, 2-ethoxyethanol, 2-(ethenyloxy)-ethanol, 1,2-ethandiol, 2-[2-(ethenyloxy)ethoxy]-ethanol, 2,2'-oxybisethanol, etc. Among other components of the pyrolysate are fragments containing one acid and one ethylene glycol unit, such as adipic acid ethylene glycol monoester. Some other fragments originate from the adipic acid moiety. Another important reaction during pyrolysis seems to be the formation of cyclopentanone. The reaction of formation for this compound is written below:



In conclusion, pyrolysis of poly[di(ethylene glycol) adipate] shows a variety of fragments and takes place with cleavage of both C–O and C–C bonds.

Another example of a Py-GC/MS analysis is that for a poly(4-hydroxy-2,2,6,6-tetramethyl-1-piperidinethanol-*alt*-1,4-butandioic acid) sample with $M_n = 3500$ and CAS# 65447-77-0. The pyrogram is shown in Figure 10.1.6. The pyrolysis was done at 600° C in He at a heating rate of 20° C/ms with 10 s THT. The separation was done on a Carbowax column in the same conditions as for other examples (see Table 4.2.2). The peak identification for the pyrogram shown in Figure 10.1.6 was done using MS spectral library searches only and is given in Table 10.1.5.

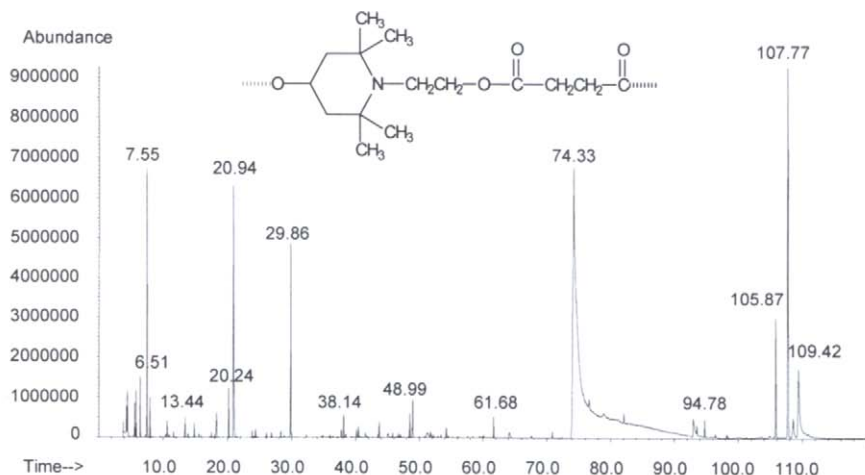


FIGURE 10.1.6. Pyrogram for a poly(4-hydroxy-2,2,6,6-tetramethyl-1-piperidinethanol-*alt*-1,4-butandioic acid) sample with $M_n = 3500$. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 10.1.5. Compounds identified in the pyrogram of poly(4-hydroxy-2,2,6,6-tetramethyl-1-piperidinethanol-*alt*-1,4-butandioic acid) sample with $M_n = 3500$ shown in Figure 10.1.6.

Peak	Compound	Ret. time	MW	Area %
1	carbon dioxide	4.37	44	0.31
2	2-methylpropene	4.54	56	1.65
3	2-methyl-1,4-pentadiene	5.67	82	0.56
4	acetaldehyde	5.88	44	0.60
5	4-methyl-1,3-pentadiene	6.51	82	0.89
6	2-methyl-1,3-pentadiene	7.55	82	4.36
7	acetone	8.04	58	0.66

TABLE 10.1.5 (continued). Compounds identified in the pyrogram of poly(4-hydroxy-2,2,6,6-tetramethyl-1-piperidinethanol-*alt*-1,4-butandioic acid) sample with $M_n = 3500$ shown in Figure 10.1.6.

Peak	Compound	Ret. time	MW	Area %
8	methanol	10.67	32	0.31
9	2,6-dimethyl-2,4-heptadiene	11.65	124	0.09
10	5,5-dimethyl-2-ethyl-1,3-cyclopentadiene	13.44	122	0.38
11	5,5-dimethyl-1-ethyl-1,3-cyclopentadiene	13.91	122	trace
12	1,1-dimethyl-2-(2-methyl-2-propenyl)cyclopropane	14.88	124	0.24
13	acetonitrile	15.56	41	trace
14	2,6-dimethyl-2,4-heptadiene	17.55	124	0.09
15	water	18.35	18	0.76
16	2,6-dimethyl-1,3,6-heptatriene	20.24	122	0.90
17	2,2,6,6-tetramethyl-1,2,5,6-tetrahydropyridine	20.94	139	6.08
18	4-methyl-3-penten-2-one	23.87	98	0.12
19	1,2-dimethylbenzene	24.44	106	0.19
20	1,6-dimethyl-1,3,6-heptatriene	26.09	122	0.09
21	3-methyl-2-butenal	28.35	84	0.11
22	2,2,5,5-tetramethyl-1,3-cyclopentadiene	29.86	122	3.76
23	2,2,3,5,5-pentamethyl-1-vinyl-3-pyrroline ?	37.80	165	0.18
24	2,2,6,6-tetramethyl-1-vinyl-1,2,5,6-tetrahydropyridine	38.14	165	0.51
25	piperidine derivative ?	40.15		0.23
26	unknown [109(100), 124(65), 67(23), 41(11), 81(10)]	40.46		0.28
27	2,6-dimethyl-2,5-heptadien-4-one ?	48.52	138	0.52
28	3-ethyl-2,4,6-trimethylpyridine	48.99	149	0.92
29	butanedioic acid dimethyl ester	54.26	146	0.17
30	unknown [109(100), 124(65), 67(23), 41(11), 81(10)]	61.68		0.39
31	2,2,6,6-trimethyl-4-piperidinol	64.20	157	0.30
32	2-(2,2,6,6-tetramethyl-1,2,5,6-tetrahydropyridyl)ethyl acetate ?	70.91	225	0.11
33	2-(2,2,6,6-tetramethyl-1,2,5,6-tetrahydropyridyl)ethyl propanoate ?	74.33	239	16.82
34	2-(2,2,6,6-tetramethyl-1,2,5,6-tetrahydropyridyl)ethan-1-ol	74.68	183	36.48
35	2-(2,2,6,6-tetramethyl-1,2,5,6-tetrahydropyridyl)ethyl propenoate ?	76.80	237	0.38
36	butanedioic acid monomethyl ester	93.02	132	0.91
37	unknown [124(100), 58(17), 256(11), 140(10), 42(4)]	94.78		0.35
38	unknown [152(100), 70(28), 153(12), 251(6), 333(5)]	105.87		3.06
39	methyl 2-[2,2,6,6-tetramethyl-(1,2,5,6-tetrahydropyridyl)ethyl] butanedioic acid ester ?	107.77	297	10.66
40	N-[(2-hydroxyethyl)] succinimide ?	108.57	143	0.95
41	unknown [170(100), 102(45), 186(38), 70(38), 296(8)]	109.42		4.61

Identification of a number of the compounds given in Table 10.1.5 is only tentative. The absence in common mass spectral libraries of the spectra for some simple compounds generated in the pyrolysate of poly(4-hydroxy-2,2,6,6-tetramethyl-1-piperidinethanol-*alt*-1,4-butandioic acid) makes it difficult to assign compounds to different peaks shown in the pyrogram from Figure 10.1.6. Two examples are the spectra tentatively assigned for 2,2,6,6-tetramethyl-1,2,5,6-tetrahydropyridine (MW = 139) and for 2,2,6,6-tetramethyl-1-vinyl-1,2,5,6-tetrahydropyridine (MW = 165), which are given in Figure 10.1.7.

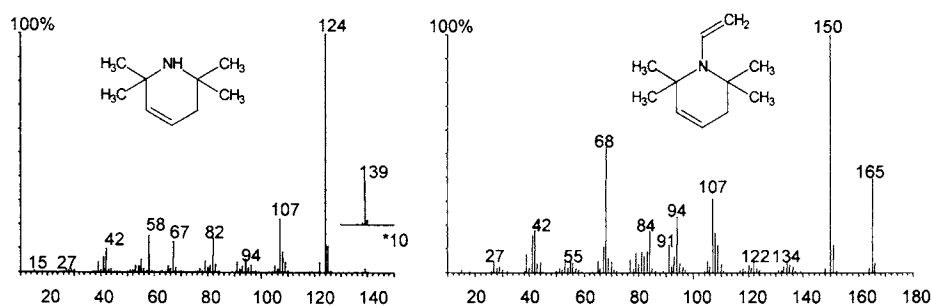


FIGURE 10.1.7. Mass spectra tentatively assigned to 2,2,6,6-tetramethyl-1,2,5,6-tetrahydropyridine (MW = 139) and 2,2,6,6-tetramethyl-1-vinyl-1,2,5,6-tetrahydropyridine (MW = 165), respectively.

Even more complicated is the assignment of the mass spectra for compounds with higher MW. The spectra assignment based on the fragmentation pattern is not always reliable, but in some instances is the only available alternative. This is the case for the spectrum of 2-(2,2,6,6-tetramethyl-1,2,5,6-tetrahydropyridyl)ethan-1-ol, which is shown in Figure 10.1.8, and for methyl 2-[2,2,6,6-tetramethyl-(1,2,5,6-tetrahydropyridyl)ethyl] butanedioic acid ester, which is shown in Figure 10.1.9.

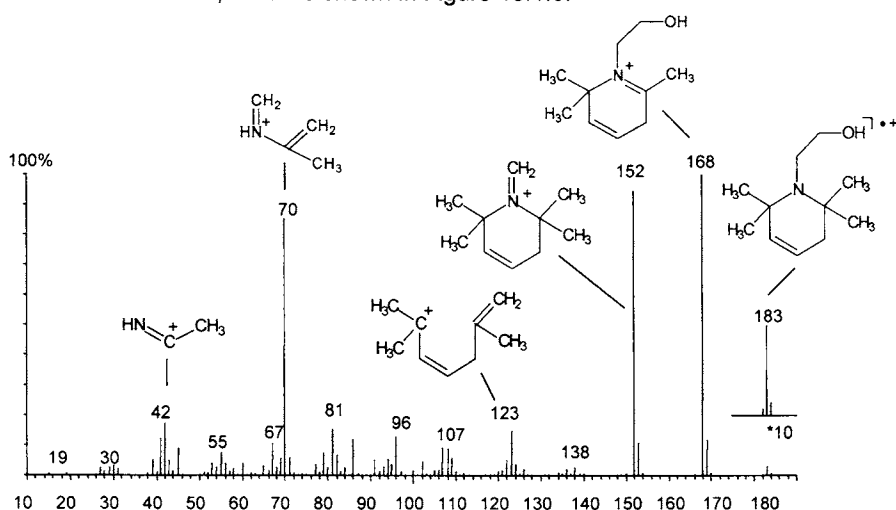


FIGURE 10.1.8. Mass spectrum tentatively assigned to 2-(2,2,6,6-tetramethyl-1,2,5,6-tetrahydropyridyl)ethan-1-ol (MW = 183).

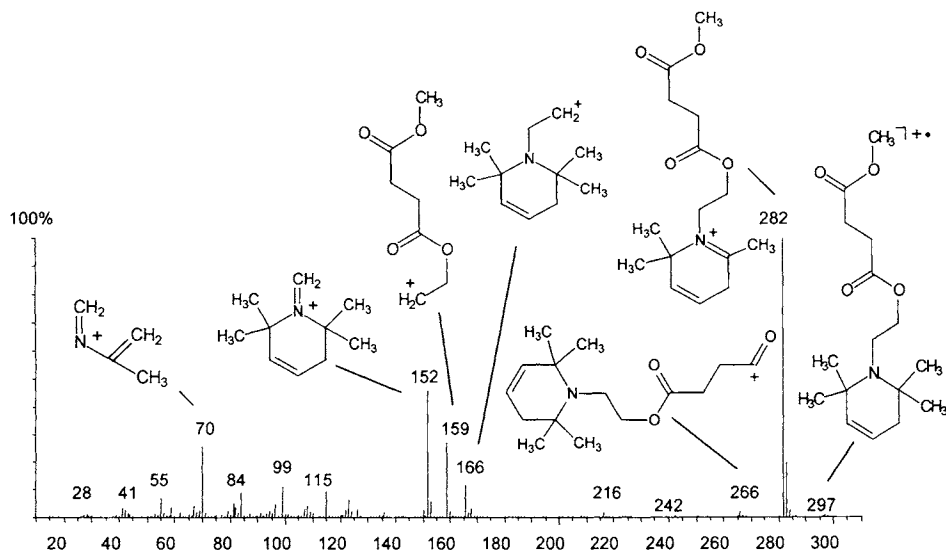
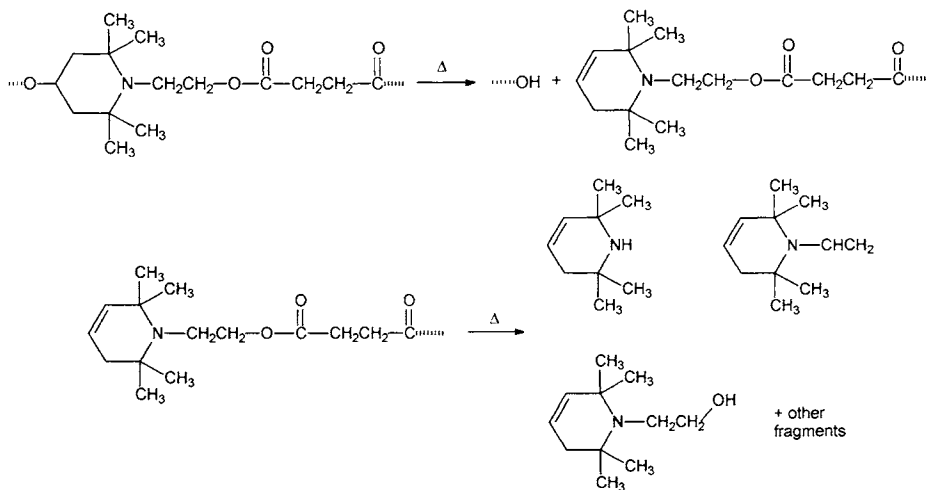


FIGURE 10.1.9. Mass spectrum tentatively assigned to methyl 2-[2,2,6,6-tetramethyl-(1,2,5,6-tetrahydropyridyl)ethyl] butanedioic acid ester (MW = 297).

Based on the molecular fragments generated during pyrolysis, it seems that several bonds are cleaved during pyrolysis. Some of possible cleavages are shown below:



The cleavage of the piperidine cycle is also a likely reaction, proven by the presence of butanedioic acid dimethyl ester and of methyl 2-[2,2,6,6-tetramethyl-(1,2,5,6-tetrahydropyridyl)ethyl] butanedioic acid ester.

- Polyesters with aromatic groups in the backbone

The polyesters with aromatic groups in the backbone have many practical applications. Among these polymers, poly(ethylene terephthalate) (PET), CAS# 25038-59-9, is probably the best known for its use in fibers for clothing, films, bottles, food containers and engineering plastics for precision-molded parts. This wide range of applications is possible because of the excellent balance of properties this material has. It can be made into articles with good clarity and dimensional stability. For packaging PET combines optimum processing, mechanical and barrier properties for retention of carbon dioxide for bottling carbonated beverages and good oxygen barrier properties that allow its use in many types of food containers. Its copolymers are used for making medical devices, toys, etc. Other esters with aromatic groups include poly(ethylene isophthalate) CAS# 26810-06-0, poly(butylene terephthalate), poly(1,4-cyclohexyldimethylene terephthalate) CAS# 100218-60-8, poly(ethylene-p-hydroxybenzoate) CAS# 25302-46-9, poly(resorcinol isophthalate) CAS# 26618-61-1, poly(hexamethylene terephthalate) CAS# 58517-23-0, etc.

A number of studies were done to assess thermal stability of aromatic polyesters. Some of these studies describe flash pyrolysis [27–32]. Some studies are dedicated to slow thermal degradation in an inert atmosphere, and others describe the decomposition in specific conditions such as in the presence of humidity or in the presence of catalysts [33]. For example, thermal decomposition of poly(butylene terephthalate) was significantly influenced by the presence of water vapor, and the amount of the residues decrease with increasing the partial pressure of water in the atmosphere [34]. In another study, thermal stability of some small molecule phthalate esters was studied [35]. The results can be used for inferring information on the thermal stability of related polymers. The influence of substitution on the β -carbon atom was evaluated on compounds such as bis(2-aminobutyl) phthalate, bis(2-nitrobutyl) phthalate, bis(2,4-diphenylbutyl) phthalate, and dineopentyl phthalate. Only the phenyl groups were found to improve the heat resistance by the obstruction of the planar configuration necessary for the *cis*-elimination and the hindrance of the formation of a six-membered cyclic transition state.

A summary regarding literature information describing the thermal decomposition of polyesters with aromatic groups in the backbone chain is given in Table 10.1.6.

TABLE 10.1.6. *Summary regarding literature information on thermal decomposition of several aromatic polyesters [12].*

Polymer	Temp. °C	Results	Ref.
poly(3-oxybenzoyl)	330	monomer, cyclic dimer to heptamer	36
poly(4-oxybenzoyl)	505–565	CO, CO ₂ , phenol, p-hydroxyphenyl benzoate	37
poly[α -ethoxycarbonyl-vinyl- ω -[4-(ethoxycarbonyl-vinyl)-phenyl]-(1,4-phenylene-2,4-bis-ethoxycarbonyl-1,3-cyclobutylene)]	320–360 for 1h in N ₂	low-molecular-weight polymer and small amount of monomer	38
poly(ethylene terephthalate)	445	pyrolysis with added CuCl ₂ does not influence the nature of degradation products, but modifies their ratio and the stability of the polymer	39

TABLE 10.1.6 (continued). Summary regarding literature information on thermal decomposition of several aromatic polyesters [12].

Polymer	Temp. °C	Results	Ref.
poly(oxydeca-methyleneoxyterephthaloyl)	ambient to 500	CO, CO ₂ , 1,9-decadiene, 1,10-decanediol, 1-decene-10-ol, benzoic acid, terephthalic acid, mono-decanyl terephthalate	40
poly(oxyethylene-oxyterephthaloyl) or poly(ethylene terephthalate)	283–306	acetaldehyde major gaseous product with CO ₂ , CO, C ₂ H ₄ , H ₂ O, CH ₄ , benzene, 2-methyl-dioxolane, terephthalic acid, and more complex chain fragments	41
poly(oxyethylene-oxyterephthaloyl) or poly(ethylene terephthalate)	900	CO, CH ₄ , CO ₂ , ethylene, acetylene, ethane, H ₂ O, propylene, ethanal, acetone, propanal, ethanol, benzene, toluene, ethylbenzene, styrene, p-vinyltoluene, benzaldehyde, p-ethyl-toluene, acetophenone, methyl benzoate, vinyl benzoate, ethyl benzoate, p-methyl-acetophenone, benzoic acid, p-methyl vinyl benzoate, p-vinylacetophenone, propyl benzoate, p-ethyl vinyl benzoate, p-vinyl vinyl benzoate, biphenyl, 1-hydroxyethyl benzoate, diacetylbenzene, p-acetyl vinyl benzoate, divinyl terephthalate, ethyl vinyl terephthalate, ethyl vinyl terephthalate, p-acetylbenzoic acid, methyl 1-hydroxyethyl terephthalate, ethylene dibenzoate	29
poly(oxyethylene-oxyterephthaloyl) or poly(ethylene terephthalate)	ambient to 500	CO, CH ₄ , CO ₂ , ethene, ketene, acetaldehyde, 1,4-dioxane, toluene, benzaldehyde, vinylbenzoate, divinylterephthalate, benzoic acid, terephthalaldehydic acid, terephthalic acid, hydroxyethyl methyl terephthalate, short chain fragments	40
poly(oxyisophthaloyl-oxy-1,3-phenylene)	330	Cyclic monomer (10 relative abundance), cyclic dimer (83.5), cyclic trimer (24.5), benzoic acid, isophthalic acid, resorcinol and various fragments of the main chain	36
poly(oxyisophthaloyl-oxy-1,4-phenylene)	330	cyclic dimer (17), cyclic trimer (4), m-phthalic acid (26), benzoic acid (7.5), hydroquinone (46), and various fragments of the main chain	36
poly(oxyterephthaloyl-oxy-1,2-phenylene)	ambient to 500	CO ₂ , benzene, phenol, benzaldehyde, catechol, cyclic dimer	42
poly(oxyterephthaloyl-oxy-1,3-phenylene)	345	cyclic dimer (2), cyclic trimer (0.3), terephthalic acid (0.4), benzoic acid (1.5), resorcinol (20) and various fragments of the main chain	36
poly(oxyterephthaloyl-oxy-1,3-phenylene)	ambient to 500	CO ₂ , benzene, phenol, benzaldehyde, biphenyl, benzoic acid, 3-hydroxyphenylbenzoate, resorcinol, mono and di(3-hydroxyphenyl) terephthalate, terephthalic acid, terephthalaldehydic acid, short chain fragments	42
poly(oxyterephthaloyl-oxy-1,4-phenylene)	350	Cyclic dimer (0.1), terephthalic acid (0.5), benzoic acid (6), hydroquinone (40.5), and various fragments of the main chain	36
poly(oxyterephthaloyl-oxy-1,4-phenylene)	ambient to 500	benzene, phenol, benzaldehyde, biphenyl, benzoquinone, 4-hydroxyphenylbenzoate, benzoic acid, mono and di(4-hydroxyphenyl) terephthalate, terephthalic acid, terephthalaldehydic acid, short chain fragments	42
poly(oxyterephthaloyl-oxy-4,4'-diphenylene)	ambient to 500	CO ₂ , benzene, phenol, benzaldehyde, biphenyl, 4-phenylphenol, p,p'-dihydroxybiphenyl, 4-hydroxybiphenylbenzoate, di(4-hydroxybiphenyl) terephthalate	42
poly(oxytetramethylene-oxy-terephthaloyl) or poly(butylene terephthalate)	240–280	butadiene, terephthalic acid, mono-3-butenyl terephthalate, and di-3-butenyl terephthalate	43
poly(oxytetramethylene-oxy-terephthaloyl) or poly(butylene terephthalate)	200–400	tetrahydrofuran, 1,3-butadiene, CO ₂ , CO, H ₂ O, benzoic acid, terephthalic acid, mono-3-butenyl terephthalic acid, toluene, phenol, benzene	44

TABLE 10.1.6 (continued). Summary regarding literature information on thermal decomposition of several aromatic polyesters [12].

Polymer	Temp. °C	Results	Ref.
poly(oxytetramethylene-oxy-terephthaloyl) or poly(butylene terephthalate)	ambient to 500	CO, CO ₂ , butadiene, tetrahydrofuran, toluene, benzene, 1,5-hexadiene, dihydrofuran, 4-vinyl cyclohexene, 1,4-butanediol, benzaldehyde, benzoic acid, terephthalaldehydic acid, terephthalic acid, mono-3-butenyl terephthalate, cyclic dimer, short chain fragments	40
polyester from terephthaloyl chloride and n=22 polyethylene glycol	ambient to 500	CO, CH ₄ (trace), CO ₂ ethene (trace), formaldehyde, acetaldehyde, 1,3-dioxalane, methoxyacetaldehyde, 1,4-dioxane, 7-membered cyclic ether, methyl benzoate, ethyl benzoate, benzaldehyde, cyclobutanone, HOCH ₂ CH ₂ OCH ₂ CHO, CH ₃ OCH ₂ CH ₂ OC ₂ H ₅ , CH ₂ =CHOCH ₂ CH ₂ OCH ₂ CHO, HO(CH ₂ CH ₂ O) ₂ C ₂ H ₅ , C ₂ H ₅ (OCH ₂ CH ₂) ₃ H, terephthalic acid, triethylene glycol, tetraethylene glycol, chain fragments	45
polyester from terephthaloyl chloride and n=4 polyethylene glycol	ambient to 500	CO, CH ₄ (trace), CO ₂ , ethene (trace), formaldehyde, acetaldehyde, 1,3-dioxalane, ethoxyacetaldehyde, 1,4-dioxane, glycidol, diethylether, 1,2-dimethoxyethane, 2-methoxyethanol, 2-ethoxyethanol, cyclobutanone, HOCH ₂ CH ₂ OCH ₂ CHO, CH ₃ OCH ₂ CH ₂ OC ₂ H ₅ , terephthalic acid, triethylene glycol, tetraethylene glycol, chain fragments	45

The analysis of alkyd resins was a subject of interest due to many practical applications of these materials [46–48]. Similar to other ester analysis, the pyrolysis with hydrolysis/alkylation, for example in the presence of TMAH, can be applied successfully for those materials [49, 50]. Pyrolysis alone is basically similar to that of other esters of aromatic diacids.

Numerous studies were done on poly(ethylene terephthalate) [51, 53]. Thermal stability of this polymer is good, as seen from the TGA curve for a poly(ethylene terephthalate) sample, CAS# 25038-59-9, with $M_w = 18,000$, shown in Figure 10.1.10. The heating for this experiment was done in air between 30° C and 830° C at a rate of 10° C/min. in air.

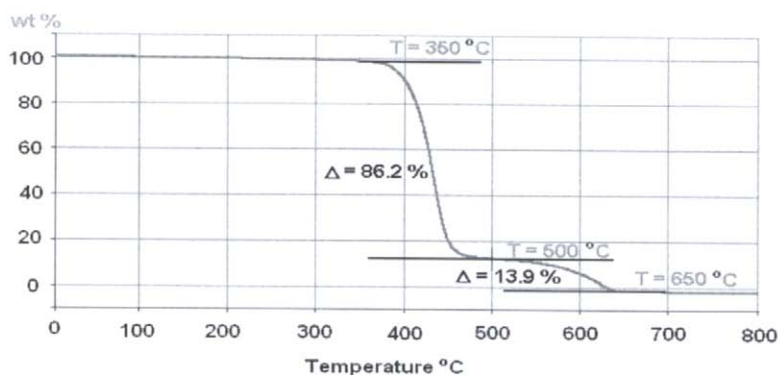


FIGURE 10.1.10. Variation of weight % loss for a poly(ethylene terephthalate) sample in a TGA experiment at a heating rate of 10° C/min.

Thermal decomposition of poly(ethylene terephthalate) starts around 350° C and leaves a char residue. The second step in the TGA curve is produced by the oxidation of the char with the oxygen present in the purging atmosphere. The results for a Py-GC/MS analysis of the same sample are shown in Figure 10.1.11. The pyrolysis was done similarly to other examples previously discussed, at 600° C in He at a heating rate of 20° C/msec with 10 sec. THT. The separation was done on a Carbowax column (60 m, 0.32 mm i.d., 0.32 µm film thickness) with the GC starting at 40° C with a ramp of 2° C/min. up to 240° C and a final oven time of 20 min. The MS was operated in EI+ mode (see Table 4.2.2). The peak identification for the chromatogram shown in Figure 10.1.11 was done using MS spectral library searches only and is given in Table 10.1.7.

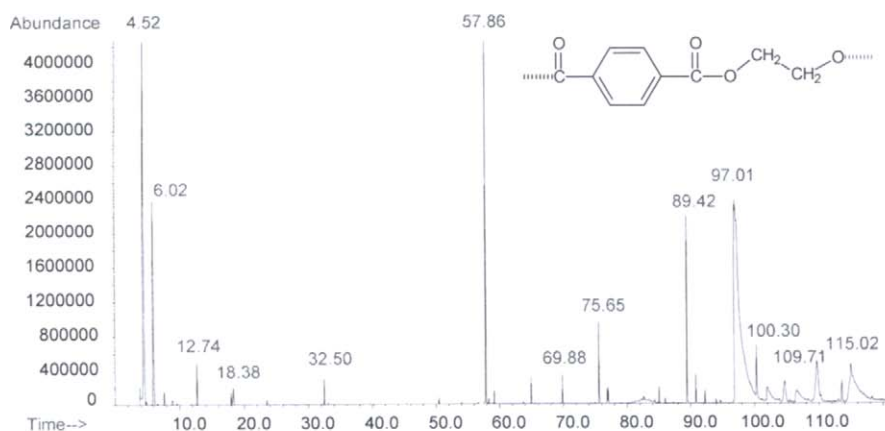


FIGURE 10.1.11. Result for a Py-GC/MS analysis of poly(ethylene terephthalate) sample $M_w = 18,000$. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

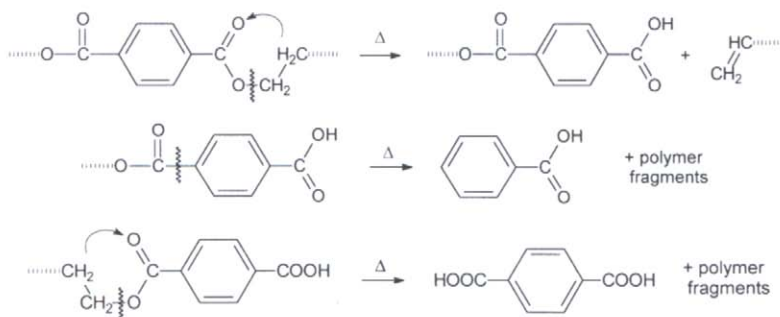
TABLE 10.1.7. Compounds identified in the pyrogram of poly(ethylene terephthalate) shown in Figure 10.1.11.

Peak	Compound	Ret. Time	MW	Area %
1	ethene	4.36	28	trace
2	carbon monoxide	4.46	28	3.11
3	carbon dioxide	4.52	44	10.22
4	acetaldehyde	6.02	44	6.44
5	furan	7.65	68	0.30
6	2-propenal	7.95	56	trace
7	benzene	12.74	78	0.82
8	toluene	18.01	92	0.26
9	water	18.38	18	0.55
10	ethylbenzene	23.55	106	trace
11	styrene	32.50	104	0.41
12	1-propenylbenzene	33.06	118	trace
13	indane	39.50	118	trace
14	benzaldehyde	50.45	106	trace
15	benzoic acid vinyl ester	57.86	148	6.87
16	1-phenyl ethanone	58.30	120	trace
17	benzoic acid ethyl ester	59.16	150	0.23

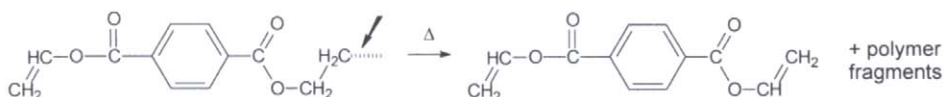
TABLE 10.1.7 (continued). Compounds identified in the pyrogram of poly(ethylene terephthalate) shown in Figure 10.1.11.

Peak	Compound	Ret. Time	MW	Area %
18	2-methyl-1-(2-methylphenyl)-1-propanone	64.96	162	0.51
19	1-(2,4-dimethylphenyl)-1-propanone	69.88	162	0.46
20	4-methyl-1-phenyl-1-penten-3-one	75.65	174	1.42
21	biphenyl	77.06	154	0.58
22	1,4-benzendicarboxylic acid divinyl ester	89.42	218	3.45
23	1,4-benzendicarboxylic acid ethyl vinyl ester	90.82	220	0.50
24	benzoic acid	97.01	122	43.21
25	benzoic acid 1-methylethyl ether	100.30	164	1.56
26	4-methylbenzoic acid	102.00	136	1.42
27	mixture	104.70		1.71
28	4-ethylbenzoic acid	106.53	150	1.87
29	mixture	109.71		4.58
30	2,2'-diformylbiphenyl ?	113.59	210	0.66
31	4-vinylbenzoic acid	115.02	148	8.87

The main pyrolysis component seen in the pyrogram is benzoic acid. However, terephthalic acid is very likely produced during pyrolysis but is not seen in the chromatogram since it does not elute from the column in the experimental conditions selected for the separation (Carbowax column). The reactions with the formation of the acids can be written as follows:



The formation of 1,4-benzendicarboxylic acid divinyl ester is also a result of a previous type of reaction as shown below:



However, the formation of CO, CO₂, acetaldehyde, 4-vinylbenzoic acid, etc. shows that in fact the pyrolytic process of poly(ethylene terephthalate) is more complex. The molecule can break in other places, and group migrations may take place during pyrolysis. Benzoic acid, for example, may be generated from terephthalic acid that suffers a partial decarboxylation.

Another polymer analyzed by Py-GC/MS is poly(1,4-butylene terephthalate) or PBT, CAS# 24968-12-5. The results for a Py-GC/MS analysis of a sample with $M_w = 38,000$ are shown in Figure 10.1.12. The pyrolysis was done at 600° C in He, similarly to other examples previously discussed (see Table 4.2.2). The peak identification for the chromatogram shown in Figure 10.1.12 was done using MS spectral library searches only and is given in Table 10.1.8.

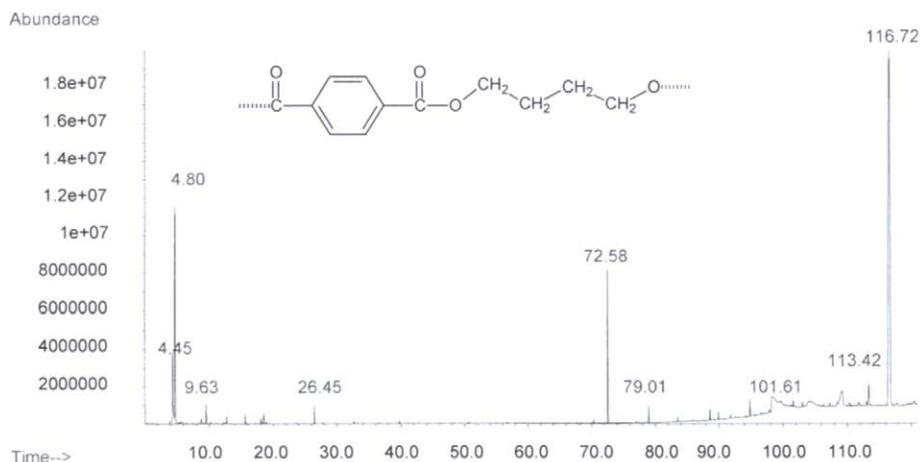


FIGURE 10.1.12. Result for a Py-GC/MS analysis of poly(1,4-butylene terephthalate) sample $M_w = 38,000$. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 10.1.8. Compounds identified in the pyrogram of poly(1,4-butylene terephthalate) sample $M_w = 38,000$ shown in Figure 10.1.12.

Peak	Compound	Ret. Time	MW	Area %
1	carbon monoxide	4.46	28	1.00
2	carbon dioxide	4.52	44	4.21
3	1,3-butadiene	4.80	54	11.11
4	2,3-dihydrofuran	8.89	70	0.32
5	tetrahydrofuran	9.63	72	1.05
6	benzene	12.79	78	0.43
7	4-ethenylcyclohexene	15.70	108	0.45
8	methylbenzene (toluene)	18.10	92	0.40
9	water	18.56	18	0.69
10	3-buten-1-ol	26.45	72	0.76
11	1,4-dimethylbenzene	27.26	106	trace
12	styrene	32.68	104	trace
13	3-butenylbenzene	39.76	132	trace
14	benzaldehyde	50.67	106	trace
15	1,4-dihydronaphthalene	56.77	130	trace
16	benzoic acid butyl ester	70.31	178	0.18
17	benzoic acid butenyl ester	72.58	176	7.66
18	biphenyl	77.33	154	trace

TABLE 10.1.8 (continued). Compounds identified in the pyrogram of poly(1,4-butylene terephthalate) sample $M_w = 38,000$ shown in Figure 10.1.12.

Peak	Compound	Ret. Time	MW	Area %
19	4-methylbenzoic acid propyl ester	79.01	178	0.75
20	4-vinylbenzoic acid butyl ester	83.52	204	0.22
21	4-vinylbenzoic acid butenyl ester	88.56	202	0.52
22	unknown (145(100), 162(33), 117(31), 115(27), 91(11))	89.91		0.44
23	unknown (159(100), 131(48), 176(21), 115(17), 91(9))	91.83		0.23
24	benzoic acid	98.34	122	9.24
25	terephthalic acid methyl vinyl ester	101.61	206	0.47
26	4-methylbenzoic acid	103.08	136	2.86
27	benzenepropanoic acid ?	109.25		4.84
28	terephthalic acid dipropenyl ester	110.40	246	0.38
29	terephthalic acid methyl propyl ester	113.06	220	0.36
30	terephthalic acid butyl butenyl ester	113.42	276	1.74
31	terephthalic acid dibutylene ester	116.72	274	49.69

Pyrolysis of poly(1,4-butylene terephthalate) is in some respects similar to that of poly(ethylene terephthalate) and generates compounds such as benzoic acid, terephthalic acid dibutylene ester, probably terephthalic acid, etc. Also the formation of CO, CO₂, benzene, biphenyl, etc. is similar. On the other hand, the percentage distribution of different compounds is rather different for poly(1,4-butylene terephthalate). A relatively high level of butadiene is generated from this polymer, while in the case of PET, formation of acetylene would not be thermodynamically possible and acetaldehyde is formed. Also, the esters of terephthalic acid with C₄ alcohols are at considerably higher levels in the pyrolysate of PBT, which seems to indicate that they are more stable than the corresponding esters with C₂ alcohols in PET pyrolysate. Some of the identifications of compounds in the pyrolysate were only tentative. Even the mass spectra for terephthalic acid butyl butenyl ester and for terephthalic acid dibutylene ester are not available in common mass spectral libraries. The corresponding spectra are given in Figures 10.1.13 and 10.1.14, respectively.

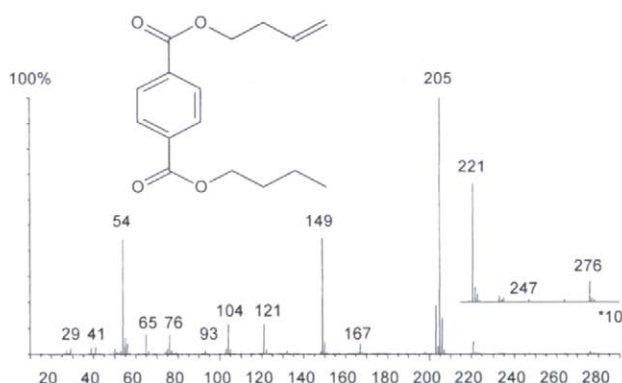


FIGURE 10.1.13. Spectrum of terephthalic acid butyl butenyl ester (MW = 276).

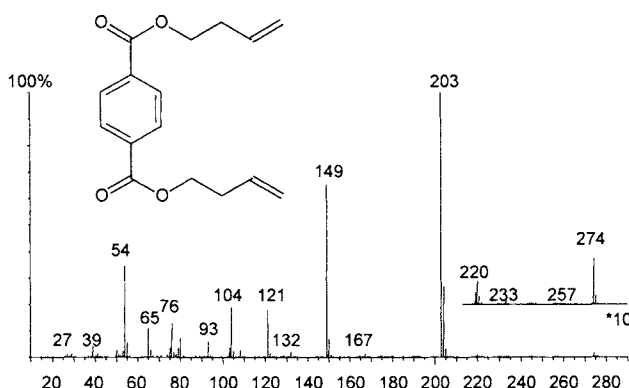
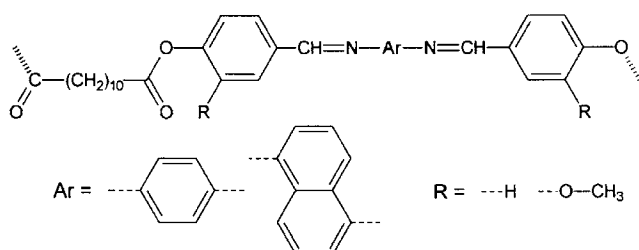


FIGURE 10.1.14. Spectrum of terephthalic acid dibutenyl ester (MW = 274).

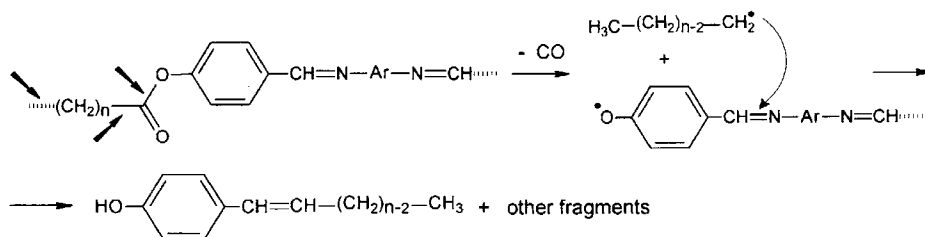
Another polyester with aromatic groups in its structure is poly(diallyl isophthalate), CAS# 25035-78-3. This polymer has a crosslinked structure and its pyrolysis products were discussed in Section 3.1. The polymer used for the Py-GC/MS experiment described in Section 3.1 had $M_w = 500,000$, and the experimental conditions were similar to those for other examples described in this book (600°C pyrolysis in He and Carbowax column separation). The main pyrolysis product was found to be 1,4-benzendicarboxylic acid di-2-propenyl ester. This compound is the homolog of terephthalic acid dibutylene ester formed in the pyrolysis of PBT.

- Other polyesters

Various literature reports offer information on thermal decomposition of other polyesters. A study has been done on thermal decomposition of poly(oxycarbonyl-1,3-phenylene-hexafluoro-iso-propylidene-1,3-phenylene-carbonyloxy-1,3-phenylene-hexafluoroisopropylidene-1,3-phenylene), which generates during heating HF (12%) and several cyclic compounds related to the polymer structure [54]. Poly(oxycarbonyl-1-chloroisopropylidene) upon heating between 253°C and 384°C generates HCl and a compound with a glycolidic structure [55]. Another study has been performed on poly(azomethine esters). These compounds have the property of forming liquid crystals but their isotropization temperature is close to the temperature of decomposition. This made necessary a thermal decomposition study. The general structure of these esters is shown below:



Ester groups in these polymers are the first affected by heating and around 300° C they start eliminating CO and CO₂. At 500° C other small molecules such as CH₄, C₂H₄, C₂H₆, C₃H₆ and C₃H₈, as well as compounds such as phenol, *p*-cresol, alkenylphenols, and several small esters are formed [56]. A cleavage of the azomethine group was not detected, these groups remaining attached to the Ar group and detected in the char by IR analysis. However, it is likely that a rearrangement takes place since long chain alkenyl phenols are detected in the pyrolysate. The suggested mechanism for the thermal decomposition of poly(azomethine esters) is shown below:



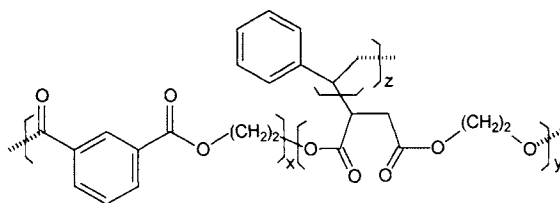
- Copolymers containing ester groups in their chain

The monomers used to generate polyesters can be used to form many copolymers that will contain ester groups. The esters can be included in copolymers with other esters, with ether groups, amides, carbonates, etc. Some examples of such copolymers are listed in Table 10.1.9.

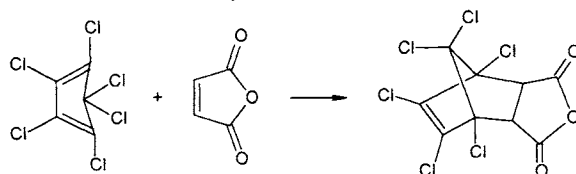
TABLE 10.1.9. Some examples of copolymers formed by esters.

Copolymer type	Examples
ester-co-ester	poly(α -hydroxybutyrate-co- α -hydroxyvalerate)
ester-co-ester	poly(4-hydroxybenzoate-co-2-oxy-6-naphthoyl)
ester-co-ester	poly(1,3-benzenedicarboxylic acid-co-1,1'-biphenyl-4,4'-diol-co-4-hydroxybenzoic acid)
ester-co-ester	poly(1,4-benzenedicarboxylic acid-co-1,1'-biphenyl-4,4'-diol-co-4-hydroxybenzoic acid)
ester-co-ester	poly(4-hydroxybenzoate-co-6-hydroxy-2-naphthalenecarboxylate)
ester-co-ester	poly(lactic acid-co-glycolic acid)
ester-co-carbonate	poly[bisphenol A-co-1,3-benzenedicarboxylic acid-co-carbonic acid]
ester-co-carbonate	poly[bisphenol A-co-1,4-benzenedicarboxylic acid-co-carbonic acid]
ester-co-carbonate	poly[bisphenol A-co-1,4-benzenedicarboxylic acid-co-1,3-benzenedicarboxylic acid-co-carbonic acid]
ester-co-amide	nylon 6-co-polyethylene terephthalate

Copolymers of polyesters are of considerable practical interest since clothing and upholstery are frequently made from polyester fibers. Also, a special group of copolymers is that of polyester thermosets. The initial material for a thermoset is a low molecular weight polyester which includes an unsaturated acid. It is possible that the unsaturated acid (frequently maleic acid) is not the only acid used for making the ester, and a saturated acid plus an unsaturated acid are used to form a copolymer. The low molecular weight polyester is further involved in a polymerization reaction of its double bonds with a vinyl component such as styrene. Several diols can be used for thermoset preparation, including 1,2-ethandiol, 1,3-propandiol, 1,4-butandiol, 1,6-hexandiol, diethyleneglycol, triethyleneglycol, etc. Anhydrides of phthalic acid, isophthalic acid, terephthalic acid in combination with maleic anhydride are used to provide the acid moiety in the thermosets. A thermoset made from 1,2-ethandiol, maleic anhydride, phthalic anhydride and styrene will have the following idealized structure:



Some thermosets are made with maleic anhydride only, or with other unsaturated 1,2-dicarboxylic acids or anhydrides such as itaconic acid or methylenesuccinic acid [7], chlorendic acid or 1,4.5.6,7,7-hexachloro-5-norbornene-2,3-dicarboxylic acid (or anhydride), 1,4.5.6,7-pentachloro-5-norbornene-2,3-dicarboxylic acid anhydride or 1,4.5.6-tetrachloro-5-norbornene-2,3-dicarboxylic acid anhydride. These norbornene derivatives can be obtained from the Diels-Alder condensation of the chlorinated cyclopenta-1,3-dienes and maleic anhydride, as shown in the following reaction:



The resulting anhydride can form polyesters with diols, and further form a thermoset by polymerization with styrene.

Thermosets are obtained in practice in two or more stages depending on the reactivity of the acids used to make the low molecular weight polyester. The last stage is the addition of styrene. Various inhibitors such as tert-butylhydroquinone (TBHQ) are added to maintain the mixture thermoplastic. A curing cycle using mild heating, initiators (such as peroxides), and accelerators (such as cobalt naphthalenate) follows the synthesis. The thermosets have many practical applications as coatings and in the manufacturing of sheets for floor covering and sanitary objects.

Thermal decomposition of polyester copolymers is of considerable interest because of their common use in practice. A number of reports are available in literature describing either pyrolysis or slow thermal decomposition of polyester copolymers [57–60], etc. Some of these reports are summarized in Table 10.1.10.

TABLE 10.1.10. Summary regarding literature information on thermal decomposition of several copolymers of esters [12].

Polymer	Temp. °C	Results	Ref.
polyester from maleic anhydride, hexolic acid and butanediol 1/1/2.2 mole ratio	100–440	tetrahydrofuran, 1-butanol, toluene, maleic anhydride, chlorosuccinic acid isomers, chlorovalerolactone isomers, hydroxypyran, allylpyran, trichlorocyclopentadiene, tetrachlorocyclopentadiene, pentachlorocyclopentadiene, hexachlorocyclopentadiene, phthalic anhydride, 1,4-butanediol, 1,4-butanediol dibenzoate, benzoic acid, 4-cyclohexene-1,2-dicarboxylic acid anhydride, benzoic acid butenyl ester, cyclohexadiene carboxylic acid propyl ester, hexolic anhydride, unidentified butenyl ester, compound containing C ₅ HCl ₅ unit, CH ₃ CH=CHCH ₂ CH ₃ , CH ₃ CH=CHCH ₂ OCH=CH ₂ , ClCH=CHOCH ₂ CH ₃	61
polyester from maleic anhydride, phthalic anhydride and butanediol 1/1/2.2 mole ratio	100–440	tetrahydrofuran, 1-butanol, 3-butene-1-ol, toluene, maleic anhydride, phthalic anhydride, 1,4-butanediol, 1,4-butanediol dibenzoate, phthalic acid butenyl ester, various esters containing butenyl, maleate and phthalate units, CH ₃ CH=CHCH ₂ OCH ₃ , CH ₃ CH=CHCH ₂ OCH=CH ₂	61
polyester from orthophthalic acid, propane diol, fumaric acid crosslinked with styrene	800	toluene, styrene, (1-methylethenyl)benzene, benzoic acid, 1,2-benzenedicarboxylic acid anhydride	62
unsaturated polyester resin: maleic acid, phthalic acid, dibromoneopentyl glycol, styrene	300–800	ethane (above 500° C), propionaldehyde (above 400° C), styrene (major product), phthalic anhydride (major product), benzene (above 500° C), toluene (above 500° C), xylene (above 500° C)	63
unsaturated polyester resin: maleic acid, phthalic acid, propylene glycol, styrene	300–800	ethane (above 600° C), propionaldehyde (above 400° C), styrene (major product), phthalic anhydride (major product), benzene (above 450° C), toluene (above 500° C), xylene (above 400° C)	63
unsaturated polyester resin: maleic acid, tetrabromophthalic acid, phthalic acid, propylene glycol, styrene	300–800	styrene (major product), phthalic anhydride (major product), benzene (above 550° C), toluene (above 450° C), xylene (above 500° C)	63

An example of a Py-GC/MS analysis of a sample of poly[butylene terephthalate-co-poly(butylene glycol) terephthalate] is shown in Figure 10.1.15. The pyrolysis was done in similar conditions as for other examples, at 600° C in He at a heating rate of 20° C/ms. with 10 s THT. The separation was done on a Carbowax column with the GC starting at 40° C with a ramp of 2° C/min. up to 240° C and a final oven time of 20 min. (see Table 4.2.2). The peak identification for the pyrogram from Figure 10.1.15 is given in Table 10.1.11.

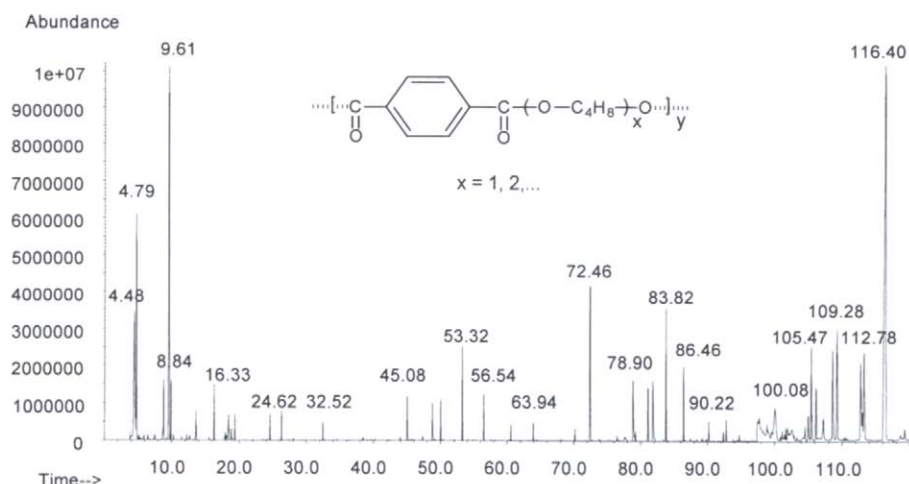


FIGURE 10.1.15. Result for a Py-GC/MS analysis of a poly[butylene terephthalate-co-poly(butylene glycol) terephthalate] sample. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

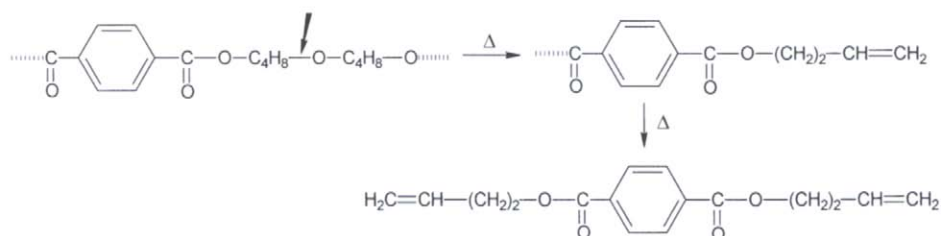
TABLE 10.1.11. Compounds identified in the pyrogram of a poly[butylene terephthalate-co-poly(butylene glycol) terephthalate] sample shown in Figure 10.1.15.

Peak	Compound	Ret. time	MW	Area %
1	butane	4.48	58	6.10
2	1,3-butadiene	4.79	54	5.94
3	octane	7.53	114	trace
4	1-octene	8.71	112	0.15
5	2,3-dihydrofuran	8.84	70	1.49
6	tetrahydrofuran	9.61	72	11.12
7	butanal	9.95	72	1.30
8	3-butenyl propyl ether	11.58	114	trace
9	2,5-dihydrofuran	12.28	70	trace
10	benzene	12.79	78	trace
11	1,1'-oxybisbutane	13.66	130	0.60
12	4-ethenylcyclohexene	15.63	108	trace
13	4-butoxy-1-butene	16.33	128	1.18
14	butenal	17.96	70	trace
15	toluene	18.26	92	trace
16	2-methylpropenal	18.49	70	1.01
17	cyclopropanecarboxaldehyde	18.87	70	0.25
18	1-but-3-enyloxybut-3-ene	19.39	126	0.53
19	1-butanol	24.62	74	0.54
20	3-buten-1-ol	26.34	72	0.61
21	styrene	32.52	104	0.40
22	1-(4-butoxybutoxy)ethene ?	45.08	172	1.03
23	2-butyltetrahydrofuran	48.87	128	0.93
24	1,4-dibutoxybutane	50.07	202	0.83

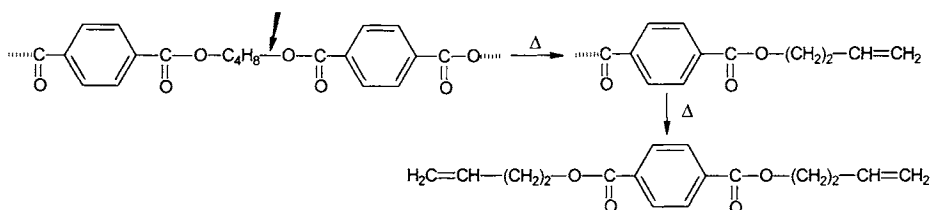
TABLE 10.1.11 (continued). Compounds identified in the pyrogram of a poly[butylene terephthalate-co-poly(butylene glycol) terephthalate] sample shown in Figure 10.1.15.

Peak	Compound	Ret. time	MW	Area %
25	1-(4-butoxybutoxy)but-3-ene	53.32	200	1.98
26	1-(4-but-3-enyloxybutoxy)but-3-ene	56.55	198	0.94
27	4-butoxy-1-butanol	60.61	146	0.30
28	4-but-3-enyloxy-1-butanol	63.95	144	0.35
29	benzoic acid butyl ester	70.20	178	0.29
30	benzoic acid butenyl ester	72.46	176	3.94
31	4-(4-butoxybutoxy)butan-1-ol	78.90	218	2.27
32	1-butoxy-4-(4-butoxybutoxy)butane	81.15	274	1.16
33	4-(4-but-3-enyloxybutoxy)butan-1-ol	81.87	216	2.42
34	1-butoxy-4-(4-butoxybutoxy)but-3-ene	83.82	272	2.97
35	1-[4-(4-but-3-enyloxybutoxy)butoxy]but-3-ene	86.46	270	1.67
36	benzoic acid	97.58	122	1.01
37	4-[4-(4-butoxybutoxy)butoxy]butan-1-ol	105.03	290	1.11
38	1,4-bis(4-butoxybutoxy)butane	105.47	346	3.45
39	4-[4-(4-but-3-enyloxybutoxy)butoxy]butanol	106.19	286	1.58
40	terephthalic acid methylbutenyl ester ?	107.24	248	1.02
41	4-(4-but-3-enyloxybutoxy)-1-(4-butoxybutoxy)butane	108.63	344	3.65
42	1,4-bis(4-but-3-enyloxybutoxy)butane	109.28	342	3.94
43	butoxy type ether ?	112.79		3.30
44	terephthalic acid dibutyl ester	113.03	278	1.07
45	terephthalic acid butyl butenyl ester	113.29	276	3.51
46	terephthalic acid dibutylene ester	116.40	274	24.08

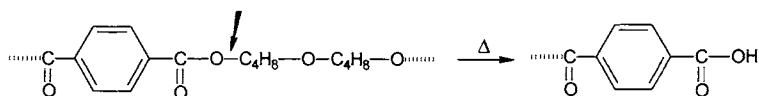
The information given in Table 10.1.11 indicates that, basically, two types of compounds are generated during the pyrolysis of this copolymer. One type is generated from the cleavage of the ester bonds in a process similar to that occurring during the pyrolysis of poly(ethylene terephthalate) or poly(1,4-butylene terephthalate). The other type is generated from the cleavage of the ether bonds of poly(butylene glycol) moiety, similar to those noticed for PEG, but containing four carbons instead of two carbons. Combinations of the two types of reactions are also common. Also, the same compound may be generated from the cleavage of two different types of bonds. For example, the formation of terephthalic acid dibutylene ester can occur by the cleavage of two ether groups, two ester groups, or one ether and one ester group. The cleavage of an ether group is shown in the following reaction:



The cleavage of an ester group is shown in the following reaction:

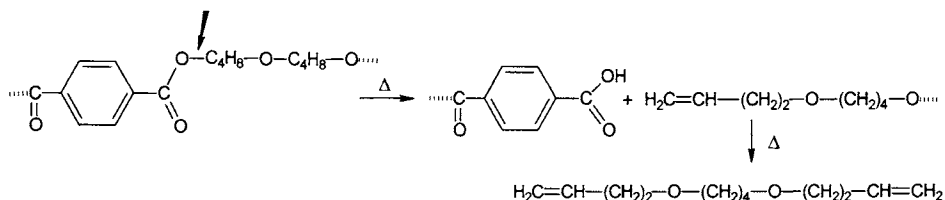


The formation of acid groups connected to a phenylene occurs similarly to the reaction shown for poly(ethylene terephthalate) and is indicated below:



The formation of benzoic acid may take place with the initial reaction that produces terephthalic acid followed by decarboxylation or directly by the cleavage of the C(O)-Ph bond.

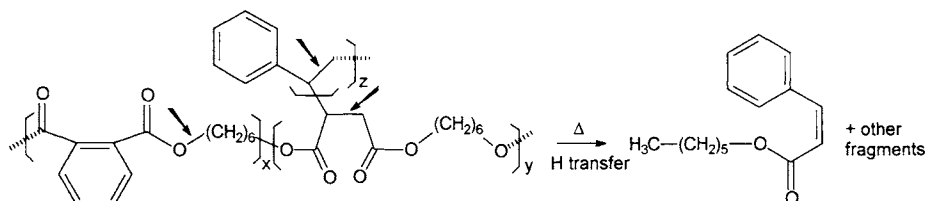
The sequences of poly(butylene glycol) generate compounds such as 1,4-dibutoxybutane, 1-(4-butoxybutoxy)but-3-ene, 1-butoxy-4-(4-butoxybutoxy)butane, 4-(4-but-3-enyloxybutoxy)butan-1-ol, etc. This type of reaction is exemplified for the formation of 1-(4-but-3-enyloxybutoxy)but-3-ene:



The complexity of reactions that are possible during the pyrolysis of this copolymer explains why the pyrogram shown in Figure 10.1.15 is more complicated than that of two chromatograms combined, namely that of poly(1,4-butyleneterephthalate) shown in Figure 10.1.12 and that of poly(tetramethyleneglycol) shown in Figure 9.1.13.

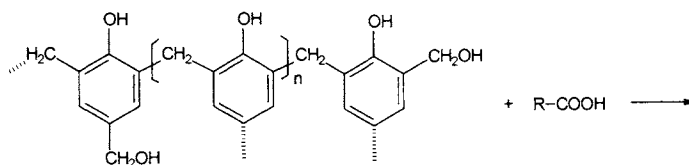
Polyesters also are used in various polymer blends such as polycarbonate/poly(butylene terephthalate), poly(butylene terephthalate/acrylonitrile-styrene-acrylic) blends, poly(vinyl chloride)/poly(ethylene terephthalate), etc. Pyrolysis results on poly(vinyl chloride)/poly(ethylene terephthalate) have been reported [64] showing that the two components influence each other, chloroesters of terephthalic and benzoic acids being found in the pyrolysate.

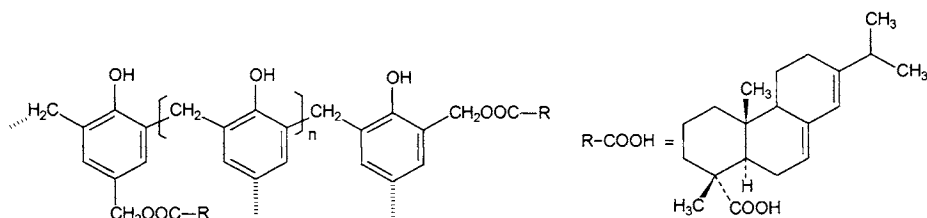
An extensive study on polyesters thermosets pyrolysis has been reported [65]. This study has been done on 13 various thermosets made with C₂, C₃, C₄, C₆ diols, maleic anhydride, the anhydrides of 1,2-, 1,3- and 1,4-phthalic acids, and styrene. Each material was pyrolyzed at 600° C for 20 s, at a heating rate of 20° C/msec. The pyrolysates were analyzed by on-line GC/MS. As an example, the compounds detected in the pyrolysate of the thermoset made from propylene glycol/maleic anhydride/phthalic anhydride/styrene were identified the following compounds: acetaldehyde, acetone, allyl alcohol, propylene glycol toluene, maleic anhydride, ethylbenzene, styrene, benzaldehyde, α -methylstyrene, phenylacetaldehyde, phthalic anhydride, dimethylphthalate, cinnamaldehyde, 1,3-diphenylpropane, styrene dimer, styrene trimer. All components in the thermoset were represented by small molecules in the pyrolysate. Some of the thermosets generated specific cinnamates, their formation being characteristic for the junction of styrene moiety with the maleic acid unit. For example, the thermoset made with 2,2-dimethyl-1,3-propandiol as the diol generated 2,2-dimethylpropylhexyl cinnamate, the thermoset made with 1,6-hexanediol generated hexyl cinnamate, etc. The formation of hexyl cinnamate from a corresponding thermoset is shown in the following scheme (the arrows show the breaking bonds):



In the analysis of the pyrolysates of these types of compounds, the generation of very polar molecules such as phthalic acids is sometimes difficult to detect. Their formation by pyrolysis is very likely, but their elution from common chromatographic columns requires high temperatures, long times, and nonpolar stationary phases for the column.

Other resins with numerous practical applications are the rosin-based materials. They have commercial use in printing inks, adhesives and coatings. Rosin is a natural product obtained from the stumps of pine trees or from tapping of living trees. It is made from about 90% rosin acids and 10% neutral materials. Rosin acids include mainly abietic acid, but also pimaric, sandaraco-pimaric, palustric, isopimaric, dehydroabietic and neo-abietic acids. This material is typically esterified with glycerin or pentaerythritol, generating ester resins. One of the commercial resins uses a phenol/formaldehyde material processed at lower temperature and containing numerous OH groups. These groups can form ester bonds with the rosin acids. For example, the reaction of a phenol formaldehyde resin with abietic acid is written below:





This group of semi-synthetic resins is rather difficult to analyze by other techniques, and pyrolytic methods have been applied successfully for their analysis, either using direct pyrolysis or using pyrolysis with hydrolysis and methylation for example in the presence of TMAH [66, 67]. The pyrolysate in the presence of TMAH contains fragments of both components of the resin, including the methyl ester of abietic acid and various methylated phenols.

Pyrolysis results for other thermosets such as those derived from chlorendic acid also are reported in literature [68, 69].

References 10.1

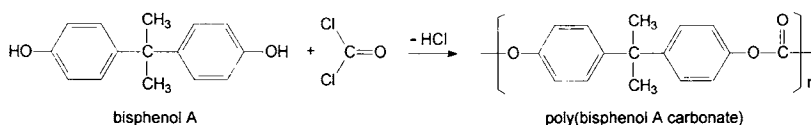
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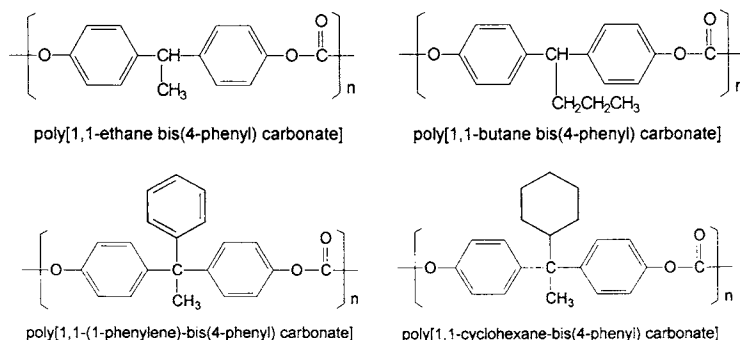
CHAPTER 11

*Poly(carbonates) and Poly(anhydrides)***11.1 POLY(CARBONATES)****- General aspects**

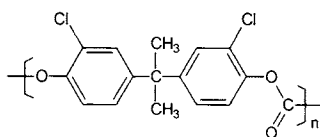
Poly(carbonates) are polymers with good mechanical properties that make them useful for being used in many household and consumer articles such as appliances, automotive parts, sporting goods, packaging, eyeglass lenses, etc. The chemical structure of these polymers is characterized by the presence of the carbonate group —O—C(O)—O— in their backbone. Typically, relatively large aromatic and aliphatic moieties are also present in the polymer. For example, poly(bisphenol A carbonate) or poly[oxy-carbonyloxy-1,4-phenylene(1-methylethylidene)-1,4-phenylene], CAS# 24936-68-3, contains two aromatic rings and one aliphatic carbon in the chain in addition to the carbonate group. This polymer can be obtained from the reaction of bisphenol A (in alkaline solution or suspension) with phosgene, as shown below:



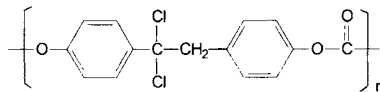
In practice, the polycarbonate initially formed has a low DP and is transformed into a high DP polymer by heating with catalysts such as tertiary amines. Instead of bisphenol A other bisphenols can be used in the same reaction. Among these are bisphenol E, G, P, etc. Some polycarbonates with structures similar to that of the polycarbonate obtained from bisphenol A are shown below:



Halogenated bisphenol derivatives can be used for the formation of polycarbonates. For example, bisphenol AF can be used instead of bisphenol A, giving poly[oxy-carbonyloxy-1,4-phenylene(hexafluoroisopropylidene)-1,4-phenylene]. The formulas for two other halogenated polycarbonates are shown below:

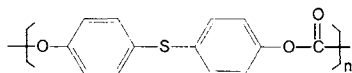


poly[2,2-propane bis[4-(2-chlorophenyl) carbonate]

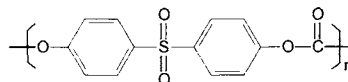


poly[1,1-dichloroethylene bis(4-phenyl) carbonate]

Isopropylidene group in bisphenol A can be replaced with sulfonyl (like in bisphenol S) or thio, the structures of the resulting polycarbonates being shown below:

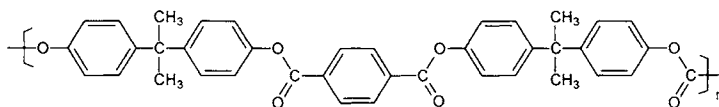


poly[thio bis(4-phenyl) carbonate]



poly[sulfonyl bis(4-phenyl) carbonate]

Other carbonates include an ester group in their structures, such as bisphenol A-terephthalic acid polyester carbonate shown below:



poly(bisphenol A-1,4-benzendicarboxylic acid polyester carbonate)

(Isophthalic acid can replace terephthalic acid in this polymer.) Less common than polycarbonates obtained from bisphenols are aliphatic type polycarbonates. One polymer of this type is poly(hexamethylene carbonate) diol with the formula $\text{HO}[-\text{CH}_2(\text{CH}_2)_4\text{CH}_2\text{OCOO}-]_n\text{CH}_2(\text{CH}_2)_4\text{CH}_2\text{OH}$ and CAS# 61630-98-6. Polycarbonates also are used in copolymers or as crosslinking bridges for vinyl polymers. For example, allyloxycarbonyloxyethyl allyloxyformate can be used for the crosslinking of polyacrylates and other vinyl polymers.

Polycarbonates are relatively resistant to heating. The thermal decomposition may take place either by an ionic ester interchange route or by free radical scission [1–4]. The study of thermal and thermoxidative decomposition processes of poly(bisphenol A carbonate) (PC) was done by matrix assisted laser desorption/ionization time of flight (MALDI-TOF) and FAB mass spectroscopic techniques [5]. PC samples were subjected to thermal degradation (under inert atmosphere) by heating at 300° C, 350° C, 400° C and 450° C. The MALDI mass spectra of the pyrolysis residues obtained at 300° C showed only a progressive reduction of the abundance of cyclic oligomers and an increase of the molar mass of the PC sample most likely due to post-condensation polymerization reactions. These findings were in agreement with other reports [6, 7] showing that the decomposition products below 400° C consist of cyclic dimers, cross-linked species, and CO₂. The decomposition mechanism seems to depend on the temperature and heating rate. At 350° C the occurrence of an extensive hydrolysis reaction producing phenol groups was observed. PC chains terminated with phenol groups together with chains bearing phenyl and isopropenyl end groups were observed at 400° C. Condensed aromatic compounds such as xanthenes also were detected in the MALDI spectra of PC samples heated at 400° C, and they are the most intense

species at 450° C. The FAB-MS spectrum of the pyrolysis residue obtained at 400° C subjected to an aminolysis reaction showed the presence of compounds containing several consecutive xanthone units. These units undergo cross-linking processes, leading to a graphite-like charred residue, as the temperature increases. Other studies [8, 9] also showed that above 420° C, at a slow heating rate, a complex series of degradations occur, resulting in branching, cross-linking, formation of esters, ethers and unsaturated compounds. Above 500° C, most functionality of the original polymer is removed with the formation of aromatic compounds, leading to extensive carbonization above 540° C. Maximum rate of decomposition for PC in N₂ is around 470°. Other similar carbonates have about the same temperature of decomposition [1, 8–11]. The char yield at 800° C in N₂ and in the presence of a fire retardant is about 27% [12]. The thermoxidative degradation of PC performed by heating the samples in air at 300° C for 30, 60, 90, 120, 150 and 180 min. produced a reduction of the PC molar mass [5]. The MALDI mass spectra of thermally oxidized PC samples at 300° C for 90 and 180 min. showed the presence of PC chains terminated with methyl-ketone, phenyl and phenol groups, most likely formed by the oxidative degradation of the isopropylidene bridge of bisphenol A units. The presence of dehydrogenated structures containing biphenyl linkage may account for the insoluble residue produced in these conditions. Thermal decomposition products in an inert atmosphere reported in literature for some polycarbonates are given in Table 11.1.1 [13].

TABLE 11.1.1. *Summary regarding literature information on thermal decomposition of several polycarbonates [13].*

Polymer	Temp. °C	Results	Ref.
poly(2-phenyltrimethylene carbonate)	ambient to 500	CO, CO ₂ , H ₂ O (possibly desorbed), α -methylstyrene, chain fragments (85%, w/w)	14
poly(neopentylene carbonate)	ambient to 500	CO ₂ , monomer, oligomer	14
poly(oxycarbonyl-oxy-1,3-phenylene)	270	cyclic trimer, tetramer, and pentamer, and various chain fragments	10
poly(oxycarbonyl-oxy-1,4-phenyleneisopropylidene-1,4-phenylene)	300–389	major products include CO ₂ , bisphenol A; minor products: CO, CH ₄ , 4-alkyl phenols	15
poly(oxycarbonyl-oxy-1,4-phenyleneisopropylidene-1,4-phenylene)	200–400	CO, CO ₂ , CH ₄ , phenol, diphenyl carbonate, 4-(4-hydroxyphenyl)-2-phenyl propane	16
poly(oxycarbonyl-oxy-1,4-phenyleneisopropylidene-1,4-phenylene)	290	cyclic dimer, cyclic trimer, bisphenol A, and other chain fragments	10
poly(oxycarbonyl-oxy-1,4-phenyleneisopropylidene-1,4-phenylene)	ambient to 500	CO, CH ₄ , CO ₂ , H ₂ O, phenol, p-cresol, p-ethylphenol, p-isopropylphenol, p-vinylphenol, bisphenol A, cyclic dimer, chain fragments including some ester structures	17
poly(oxycarbonyl-oxy-1,4-phenyleneisopropylidene-1,4-phenylene)	300	phenol, p-cresol	17
poly(oxycarbonyl-oxy-1,4-phenyleneisopropylidene-1,4-phenylene)	375	CO ₂ , phenol, p-cresol	17
poly(oxycarbonyl-oxy-1,3-phenylene-hexafluoro-trimethylene-1,3-phenylene)	-	HF (3%), cyclic dimer	18
poly(oxycarbonyl-oxy-1,4-phenylene-oxycarbonyl-oxy-tetramethylene)	270	cyclic dimer and trimer, and higher cyclic fragments	10

TABLE 11.1.1 (continued). Summary regarding literature information on thermal decomposition of several polycarbonates [13].

Polymer	Temp. °C	Results	Ref.
poly(oxycarbonyloxy-1,4-phenylene-phthalidilidene-1,4-phenylene)	350	CO ₂ , CO, O ₂ , H ₂ O, phenol, fluorenone, diphenyl carbonate, xanthone, anthraquinone, 2-hydroxy-anthraquinone, 2-benzoxanthraquinone, phenolphthalein, traces of benzoxypheol and hydroquinone	19
poly(oxycarbonyloxy-1,4-phenylene-isopropylidene-1,4-phenylene-oxycarbonyl-tetramethylene)	240	cyclic monomer and dimer, and higher cyclic fragments	10
poly(trimethylene carbonate)	ambient to 500	CO ₂ , H ₂ O (possibly desorbed), trimethylene carbonate, cyclic oligomers	20
poly[oxycarbonyl-oxy-1,4-phenylene(1-phenylethylidene)-1,4-phenylene]	427	scission of carbonate bridges, CO ₂ , in air forms aldehydes, ketones, quinones.	21
poly[oxycarbonyloxy-1,4-phenylene-(dichloroethenylidene)-1,4-phenylene]	550	below 550° C produces volatile tars and fuel gases and a primary char; heating this primary char above 550° produces a carbonaceous residue, best described as a conglomerate of loosely linked small graphitic regions.	22

The results for a Py-GC/MS analysis of a poly(bisphenol A carbonate) CAS# 25037-45-0 sample with $M_w = 29,000$ are shown in Figure 11.1.1. The polymer has the idealized formula $[-OC_6H_4-4-C(CH_3)_2C_6H_4-4-OC(O)-]_n$. The pyrolysis was done similarly to other experiments previously discussed, at 600° C in He at a heating rate of 20° C/ms with 10 s THT. The separation was done on a Carbowax column (60 m, 0.32 mm i.d., 0.32 μ m film thickness) with the GC starting at 40° C with a ramp of 2° C/min. up to 240° C and a final oven time of 20 min. The MS was operated in EI+ mode (see Table 4.2.2). The peak identification for the chromatogram shown in Figure 11.1.1 was done using MS spectral library searches only and is given in Table 11.1.2.

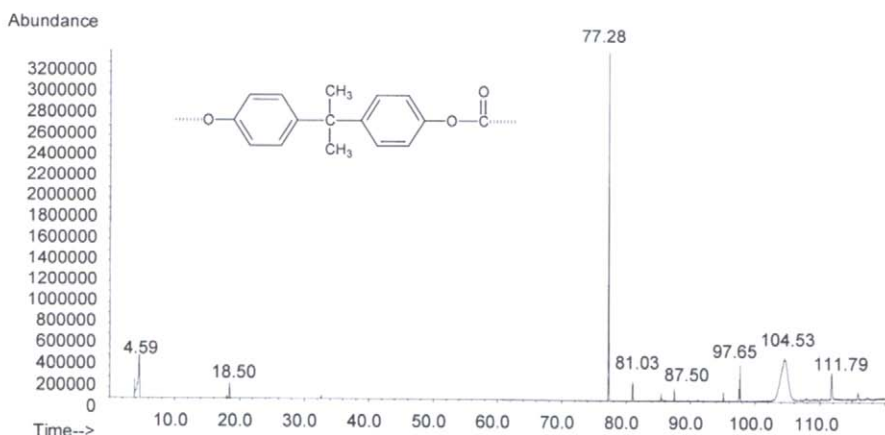
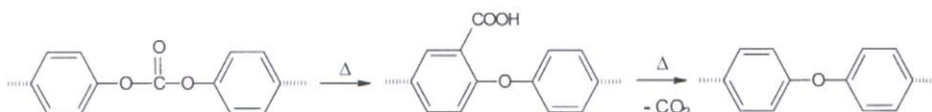


FIGURE 11.1.1. Pyrogram from a Py-GC/MS analysis of a poly(bisphenol A carbonate) sample with $M_w = 29,000$. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 11.1.2. Compounds identified in the pyrogram of a poly(bisphenol A carbonate) sample with $M_w = 29,000$ as shown in Figure 11.1.1.

Peak	Compound	Ret. Time	MW	Area %
1	carbon dioxide	4.58	44	10.22
2	toluene	18.10	92	trace
3	water	18.50	18	1.71
4	styrene	32.48	104	trace
5	phenol	77.28	94	29.62
6	4-methylphenol	81.03	108	1.42
7	4-ethylphenol	85.31	122	trace
8	4-(1-methylethyl)-phenol	87.51	136	0.93
9	ethenyloxybenzene	95.05	120	trace
10	2,3-dihydro-2-methyl-benzofuran	97.65	134	3.75
11	diethylene glycol dibenzoate (additive ?)	104.53	314	48.49
12	unknown [55(100), 83(68), 82(66), 67(52), 54(39), 101(9)]	111.79		3.87

The main decomposition product of poly(bisphenol A carbonate) during flash pyrolysis, which is detected using the separation on a Carbowax column, is phenol. Bisphenol A (which has the base peak at 213 a.u. and the molecular ion at 228 a.u.) is not detected in the pyrogram, although other studies indicate its presence in the pyrolysate as a major component. Very likely, bisphenol A does not elute in the experimental conditions used for the pyrolysate separation. A broad peak in the pyrogram tentatively identified as diethylene glycol dibenzoate may be the result of the presence of an additive. These Py-GC/MS results are in agreement with various studies on thermal decomposition of poly(bisphenol A carbonate) [16]. The formation of CO_2 in the thermal decomposition of these compounds can be explained by reactions of the type:



The ether typically continues the decomposition process, and for this reason there are similarities between the pyrolysis products of aromatic ethers and of aromatic carbonates (see Section 9.1).

A polycarbonate containing an aliphatic hydrocarbon moiety instead of an aromatic ring is poly(hexamethylene carbonate), CAS# 61630-98-6. The results for a Py-GC/MS analysis of a sample with $M_n = 860$ are shown in Figure 11.1.2. The polymer used as a sample has alcohol end groups. It is a poly(hexamethylene carbonate) diol and has the idealized formula $\text{HO}[-\text{CH}_2(\text{CH}_2)_4\text{CH}_2\text{OC}(\text{O})\text{O}]_n\text{CH}_2(\text{CH}_2)_4\text{CH}_2\text{OH}$. The pyrolysis was done similarly to other experiments previously discussed, at 600°C in He with the separation on a Carbowax column (see Table 4.2.2). The peak identification for the chromatogram shown in Figure 11.1.2 was done using MS spectral library searches only and is given in Table 11.1.3.

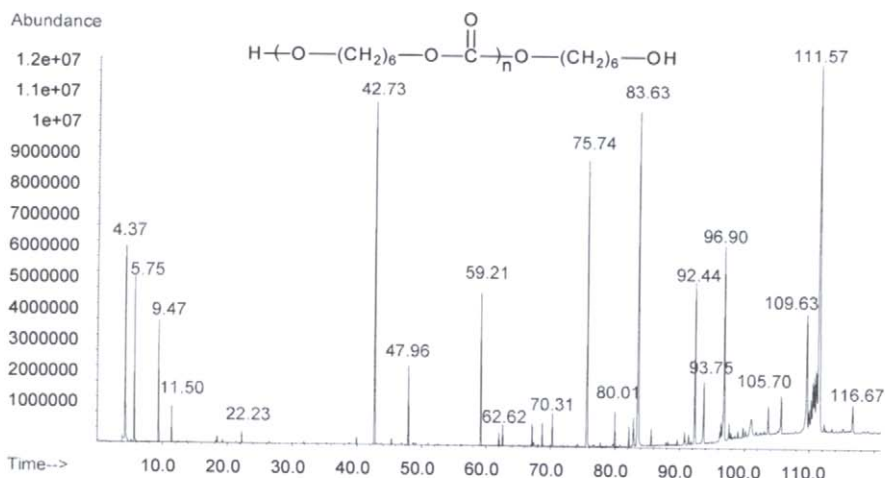


FIGURE 11.1.2. Pyrogram from a Py-GC/MS analysis of a poly(hexamethylene carbonate) diol sample with $M_n = 860$. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 11.1.3. Compounds identified in the pyrogram of a poly(hexamethylene carbonate) diol sample with $M_n = 860$ as shown in Figure 11.1.2.

Peak	Compound	Ret. Time	MW	Area %
1	carbon dioxide	4.37	44	4.87
2	1-hexene	5.30	84	trace
3	1,5-hexadiene	5.75	82	2.48
4	1,3-cyclohexadiene	9.47	80	1.89
5	1,4-cyclohexadiene	11.50	80	0.58
6	oxepane	18.46	100	0.22
7	1,4-dioxane	19.26	88	trace
8	9-oxabicyclo[6.1.0]nonane ?	22.23	126	0.19
9	cyclopentanecarboxaldehyde	26.46	98	trace
10	1-pentanol	31.78	88	trace
11	2-(ethenyloxy)-ethanol	39.98	88	0.14
12	5-hexen-1-ol	42.73	100	9.25
13	unknown carbonate	45.33		trace
14	3-cyclohexen-1-ol	47.96	98	1.56
15	unknown carbonate	59.21		2.98
16	4-methylenecyclohexanemethanol	62.02	126	0.27
17	2-[2-(ethenyloxy)ethoxy]ethanol	62.62	132	0.41
18	unknown [80(100), 81(46), 44(44), 45(40), 79(38)]	67.17		0.44
19	2,9-dimethyl-3,7-decadiene ?	68.77	166	0.43
20	unknown [42(100), 67(56), 55(44), 41(43), 71(15)]	70.31		0.72
21	unknown carbonate	75.74	154	7.91
22	unknown carbonate	80.01		0.71
23	unknown carbonate	82.22		0.43
24	2-[2-(2-vinyloxyethoxy)ethoxy]ethan-1-ol	82.89	176	0.77
25	1,6-hexandiol	83.63	118	12.01

TABLE 11.1.3 (continued). Compounds identified in the pyrogram of poly(hexamethylene carbonate) diol sample with $M_n = 860$ as shown in Figure 11.1.2.

Peak	Compound	Ret. Time	MW	Area %
26	unknown carbonate	85.64		0.43
27	2,2'-[1,2-ethandiybis(oxy)]bis-ethanol	92.44	150	4.57
28	unknown carbonate	93.75		1.71
29	unknown carbonate	96.44		0.84
30	unknown carbonate	96.90	142	6.16
31	1,4-cyclohexandimethanol	97.69	144	0.57
32	unknown [89(100), 45(28), 43(20), 28(13), 133(9)]	103.73		1.00
33	unknown carbonate	105.71		1.81
34	pentaethylene glycol	109.63	282	5.88
35	unknown carbonate	109.99		0.85
36	unknown carbonate	110.27		1.27
37	unknown carbonate	110.57		2.16
38	unknown carbonate	110.83		2.07
39	unknown carbonate	111.11		2.26
40	unknown carbonate, spectrum shown in Figure 11.1.5	111.57		19.10
41	unknown carbonate	116.67		1.07

A number of peaks in the pyrolysate of poly(hexamethylene carbonate) were fragment molecules with six carbons and containing an OH group. Among these are 5-hexen-1-ol, 3-cyclohexen-1-ol, 1,6-hexandiol. These compounds were either generated from the cleavage of the carbonate group with an oxygen retained to the hydrocarbon chain or from the six-carbon group with an alcohol end functionality. Other peaks were identified as similar to those generated from the pyrolysis of poly(ethylene glycol) and include 2-(ethenyloxy)-ethanol, 2-[2-(ethenyloxy)-ethoxy]ethanol, 2'-[1,2-ethandiybis(oxy)]bis-ethanol. The source of these compounds is not clear. They may be generated from polyether groups not expected but present in the polymer. A number of other peaks in the pyrogram are generated by compounds containing a carbonate group. However, positive identification for these peaks is difficult since the number of available mass spectra for carbonates is rather limited in commercial mass spectral libraries. One carbonate with available mass spectrum is that of carbonic acid dipentyl ester, which is shown in Figure 11.1.3.

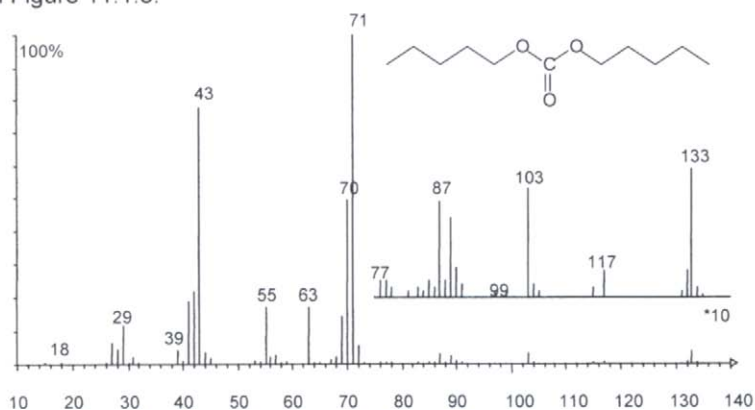
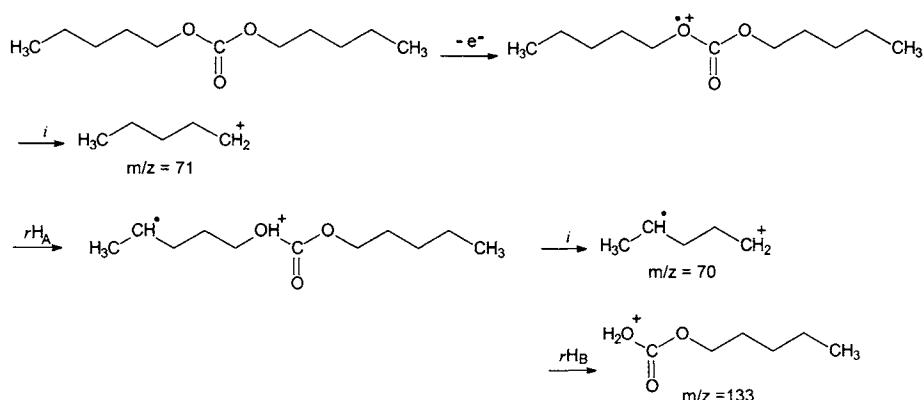


FIGURE 11.1.3. Mass spectrum of carbonic acid dipentyl ester.

Several ions in the mass spectrum of carbonic acid dipentyl ester can be explained by the reactions indicated below:



(Common notations were used in the previous reactions, such as $-e^-$ for the subtraction of an electron during the ionization process, i for the inductive cleavage, rH_A for H rearrangement with the formation of an odd electron ion, rH_B for cleavage with the H rearrangement and the formation of an even electron ion.)

The mass spectra for about 20 peaks in the pyrogram are similar to each other, and one example is given for the peak eluting at 59.21 min. This spectrum is shown in Figure 11.1.4.

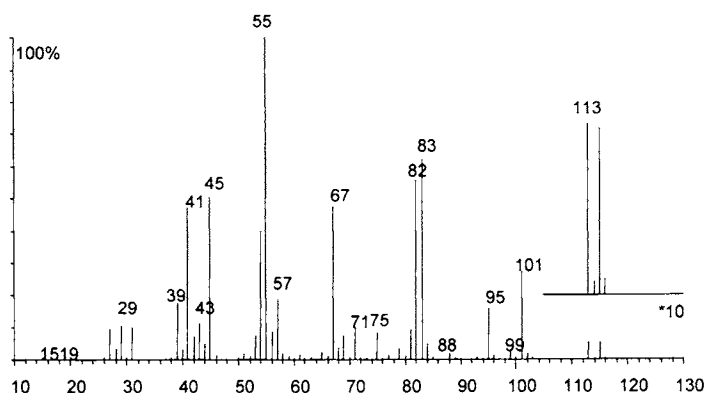
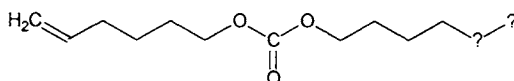
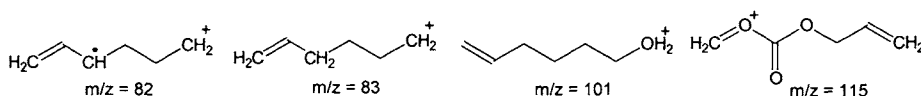


FIGURE 11.1.4. Mass spectrum for the peak eluting at 59.21 min. in the pyrogram of poly(hexamethylene carbonate), possibly of carbonic acid dihex-5-enyl ester.

The mass spectrum from Figure 11.1.4 can be tentatively assigned, by similarity with the spectrum from Figure 11.1.3, to a carbonate with the structure shown below:



The atoms or groups indicated by ? can be unsaturated carbons, carbons connected to an OH group, or carbon further connected to a carbonate group. Some of the fragment ions resulting from this compound are the following:



Another example shown in Figure 11.1.5 is the spectrum for the peak eluting at 111.57 min. in the pyrogram of poly(hexamethylene carbonate).

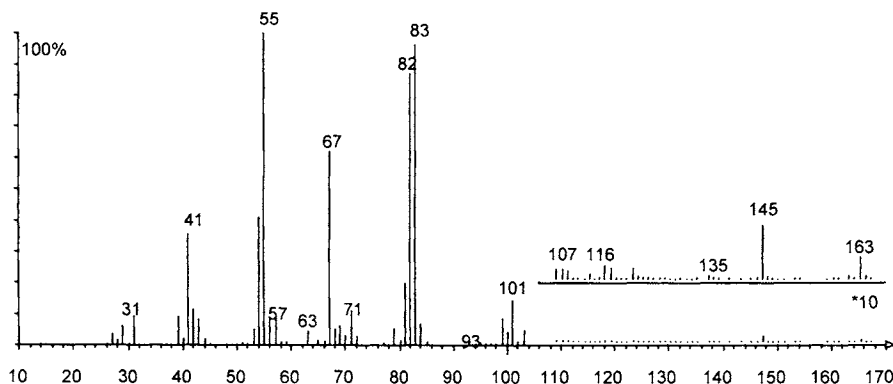
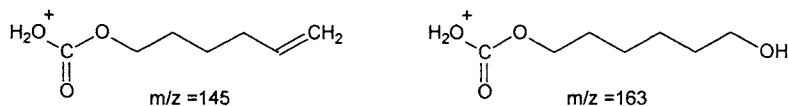


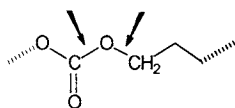
FIGURE 11.1.5. Mass spectrum for the peak eluting at 111.57 min. in the pyrogram of poly(hexamethylene carbonate), possibly of 6-hydroxyhexyl carbonate (MW = 162).

The large retention time of the compound generating the spectrum shown in Figure 11.1.5 indicates that it may belong to 6-hydroxyhexyl carbonate, or to a dimer with an OH group, or to a trimer of the hexamethylene carbonate. The ion with $m/z = 145$ is likely to be the homolog of the ion generating the ion $m/z = 133$ in the spectrum of carbonic acid dipentyl ester. The tentative structures of the ions with $m/z = 145$ and $m/z = 163$ are shown below:



Among these structures, the probability that the spectrum belongs to 6-hydroxyhexyl carbonate is higher, since the same compound is formed in the pyrolysis of poly[(1,6-hexyl-1,2-ethyl carbonate)diol 4,4'-methylenebis(phenyl isocyanate)]-co-[1,4-butanediol 4,4'-methylenebis(phenyl isocyanate)], with the pyrogram shown in Figure 11.1.6.

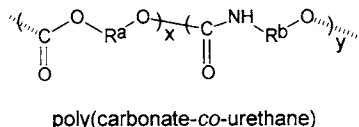
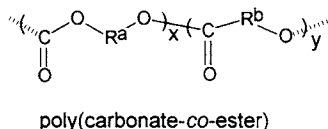
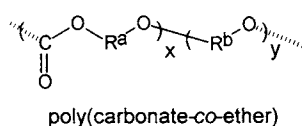
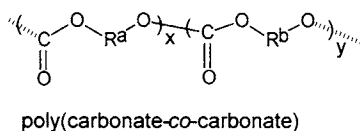
Although a sure assignment of several carbonates assumed to be present in the pyrolysate was not possible, it is likely that the pyrolysis process takes place mainly with the cleavage of C–O bonds where the carbon can be either in the aliphatic chain of the alcohol or connected to another oxygen in the carbonate group. The bonds likely to be cleaved in a carbonate are shown by arrows in the following structure:



When the carbon in the aliphatic chain retains the oxygen atom to form an alcohol, the reaction is very likely followed by CO₂ elimination.

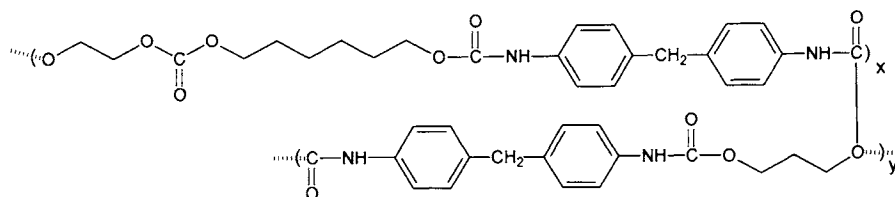
- Copolymers with carbonate groups in the backbone

Several types of copolymers have polycarbonate sequences in their structure. The copolymers can be obtained between two different carbonates, between a carbonate and an ether, a carbonate and an ester, a carbonate and an urethane, etc. Formulas of such copolymers are shown below:



Examples of copolymers with practical use between two different carbonates are poly[2,2-propanebis(4-phenyl)carbonate]-*block*-poly[2,2-propanebis[4-(2,6-dimethylphenyl)]carbonate], poly[[1,1-cyclohexane bis(4-phenyl)carbonate]-*co*-[2,2-propane bis(4-phenyl)carbonate]], and poly[[1,1-dichloroethylene bis(4-phenyl)carbonate]-*co*-[2,2-propane bis(4-phenyl)carbonate]]. Examples of copolymers between a carbonate and an ester are poly[4,4'-(1-methylethylidene)bis[phenol]-*co*-1,3-benzenedicarboxylic acid-*co*-carbonic acid], poly[4,4'-(1-methylethylidene)bis[phenol]-*co*-1,4-benzenedicarboxylic acid-*co*-carbonic acid], etc. Other known copolymers include poly[2,2-propanebis(4-phenyl)carbonate]-*block*-poly(ethylene oxide), poly[2,2-propanebis(4-phenyl)carbonate]-*block*-polysulfone, poly[2,2-propanebis(4-phenyl)carbonate]-*block*-poly(dimethylsiloxane), poly[2,2-propanebis(4-phenyl)carbonate]-*block*-poly(methyl methacrylate), etc. These copolymers have in general good thermal resilience and decompose similarly to other polycarbonates [23].

The results for a Py-GC/MS analysis of a carbonate urethane copolymer are shown below for poly[(1,6-hexyl-1,2-ethyl carbonate)diol 4,4'-methylenebis(phenyl isocyanate)]-co-[1,4-butandiol 4,4'-methylenebis(phenyl isocyanate)]. The idealized structure for this copolymer is shown below:



The polymer is available as a soft material with $M_w = 264,000$ and as a hard material with $M_w = 237,000$, depending on the proportion of the two copolymers. The pyrogram for the soft copolymer is shown in Figure 11.1.6, and the pyrogram for the hard copolymer is shown in Figure 11.1.7. The pyrolysis and pyrolysate separation were done in the same conditions as those for other examples previously discussed (see Table 4.2.2).

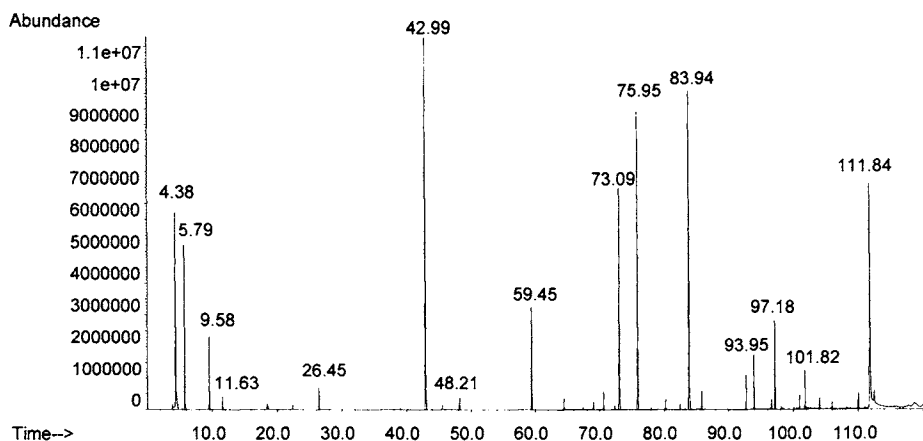


FIGURE 11.1.6. Result for a Py-GC/MS analysis of a carbonate urethane soft copolymer, $M_w = 264,000$. Pyrolysis done on 0.4 mg material at 600°C in He, with the separation on a Carbowax type column.

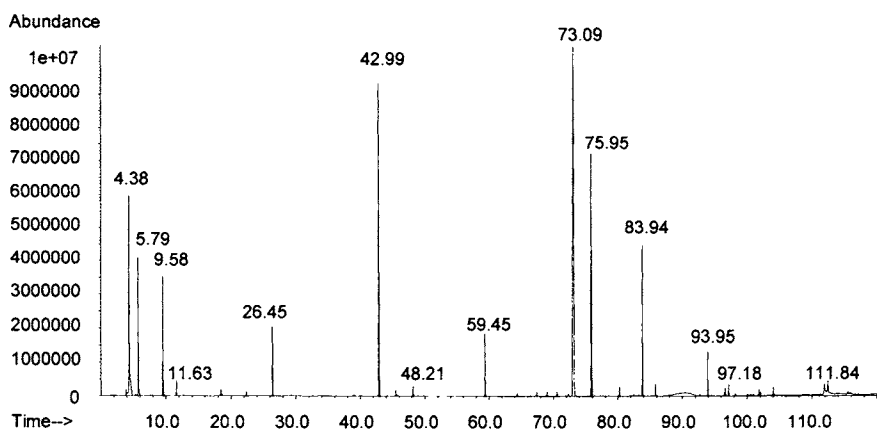


FIGURE 11.1.7. Result for a Py-GC/MS analysis of a carbonate urethane hard copolymer, $M_w = 237,000$. Pyrolysis done on 0.4 mg material at 600°C in He, with the separation on a Carbowax type column.

The peak identification obtained using MS spectral library searches only for the pyrogram shown in Figure 11.1.6 are given in Table 11.1.4. Most peaks in the two pyrograms belong to identical compounds but at different proportions in the pyrolysate.

TABLE 11.1.4. Compounds identified in the pyrogram of a carbonate urethane soft copolymer, $M_w = 264,000$ as shown in Figure 11.1.6.

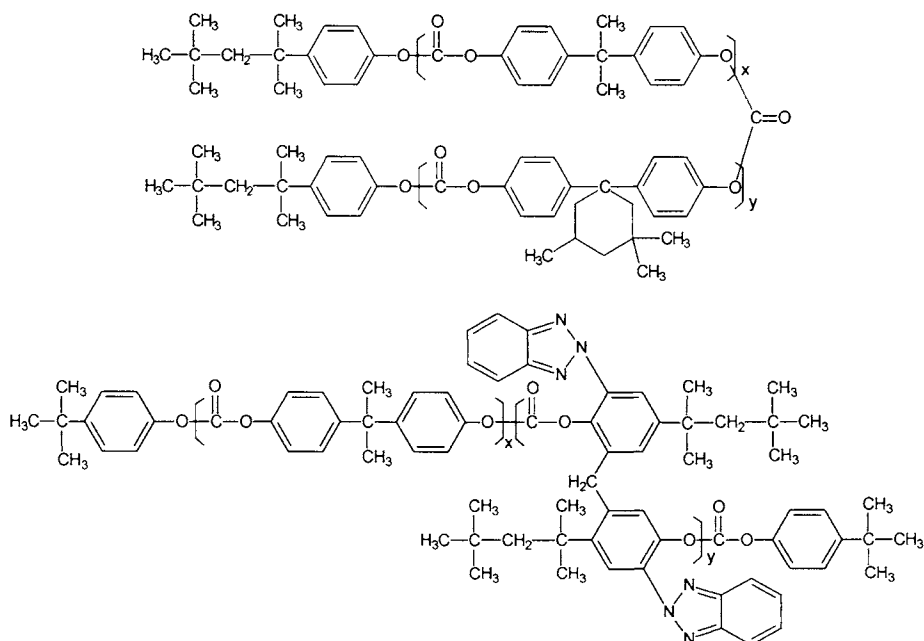
Peak	Compound	Ret. time	MW	Area %
1	carbon dioxide	4.38	44	9.06
2	1,5-hexadiene	5.79	82	4.37
3	(Z)-1,3,5-hexatriene	9.58	80	2.37
4	1,4-cyclohexadiene	11.63	80	0.37
5	water	18.32	18	trace
6	oxepane	18.62	100	0.45
7	1,4-dioxane	19.49	88	trace
8	hexanal	20.57	100	trace
9	cyclododecanone ?	22.39	182	0.21
10	2-buten-1-ol	26.45	72	0.82
11	cyclopentanecarboxaldehyde	26.63	98	trace
12	1-hexanol	39.22	102	trace
13	2-(ethenyloxy)-ethanol	40.23	88	trace
14	5-hexen-1-ol	42.99	100	15.82
15	2-propenylcyclohexane	45.51	124	0.21
16	3-cyclohexen-2-ol	48.21	98	0.51
17	3-octen-1-ol	49.32	128	trace
18	1-methyl-2-(2-propenyl)cyclohexane	59.45	124	3.58
19	2-(2-ethenyloxy)ethoxyethanol	62.90	132	0.25
20	1-cyclohexyl-1-propyne	64.46	122	0.45
21	bicyclo[2.2.2]oct-2-ene ?	67.44	108	0.25
22	2,7-dimethyl-3-vinyl-5-octene	69.01	166	0.47
23	unknown [42(100), 67(48), 55(43), 41(39), 71(13)]	70.6	142	0.98

TABLE 11.1.4 (continued). *Compounds identified in the pyrogram of a carbonate urethane soft copolymer, $M_w = 264,000$ as shown in Figure 11.1.6.*

Peak	Compound	Ret. time	MW	Area %
24	2,6-bis(1,1-dimethylethyl)-4-methylphenol (BHT) additive	72.35	220	0.39
25	1,4-butandiol	73.09	90	10.64
26	1,1'-bicyclohexyl ?	75.93	166	10.82
27	1-cyclohexylethanol	80.23	128	0.64
28	unknown [55(100), 82(60), 83(58), 89(56), 41(44), 98(18)]	82.50		0.40
29	2,2'-[oxybis(ethanedioxy)]bis-ethanol ?	83.15	194	0.45
30	1,6-hexandiol	83.94	118	13.37
31	(1-hexyl)cyclohexane ?	85.86	168	1.12
32	2,2'-[1,2-ethandiolbis(oxy)]bis-ethanol	92.73	150	1.74
33	n-nonylcyclohexane ?	93.95	210	1.76
34	propenylcyclohexane type ?	96.63	?	0.48
35	4-methyl-5-decanol	97.18	172	3.02
36	1-cyclohexylethanol type ?	98.18		0.44
37	1-cyclohexylethanol type ?	100.52		0.59
38	1-cyclohexylethanol type ?	100.97		0.92
39	unknown [55(100), 67(57), 73(56), 54(46), 82(37), 41(37)]	101.82		1.11
40	2,2'-[oxybis(ethanedioxy)]bis-ethanol type ?	110.02	196	0.72
41	unknown carbonate with spectrum identical to that shown in Figure 11.1.4, possibly 6-hydroxyhexyl carbonate	111.84	162	11.23

The results of pyrolysis for poly[(1,6-hexyl-1,2-ethyl carbonate)diol 4,4'-methylenebis(phenyl isocyanate)]-co-[1,4-butandiol 4,4'-methylenebis(phenyl isocyanate)] show that the pyrolysis process for this copolymer is in many respects similar to that of other polycarbonates. The possible formation of 4,4'-methylenebisbenzeneamine, which has the base peak at 198 a.u. corresponding to the molecular ion, and which is likely to be formed in the pyrolysate, is not detected in the pyrogram. This compound does not elute in the experimental conditions used for the pyrolysate separation, and its formation cannot be verified.

Other studies on pyrolysis of polycarbonates are reported in literature, including analytical characterizations and studies on thermal decomposition. Successful results on polycarbonate analysis were obtained using pyrolysis in the presence of a derivatizing agent such as TMAH that led to the formation of methyl esters of compounds in the pyrolysate that have acidic groups. This procedure facilitates the qualitative and quantitative analysis of certain polycarbonate copolymers [24]. For example, specific groups on polycarbonates were proven to enhance thermal stability and light stability. Thermal stability is enhanced by 3,3,5-trimethylcyclohexadienyl side groups, and light stability by 2H-benzotriazol-2-yl groups. Two copolymers with these types of groups were analyzed using pyrolysis with TMAH derivatization, with better results than by straight pyrolysis [24]. The structures of the two types of copolymers are shown below:



The pyrolysis products of copolymers with structures as shown above and having different proportions of comonomers are reported [24].

References 11.1

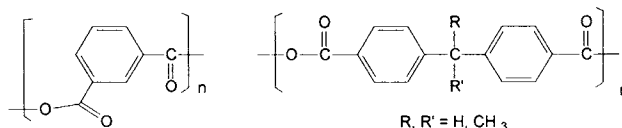
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11.2 POLY(ANHYDRIDES)

- General aspects

Poly(anhydrides) are polymers containing the group $-\text{C}(\text{O})-\text{O}-\text{C}(\text{O})-$ in their backbone. Several polyanhydrides such as poly(oxyisophthaloyl), poly(oxycarbonyl-1,4-phenylene methylene-1,4-phenylene carbonyl), poly(oxycarbonyl-1,4-phenylene isopropylidene-1,4-phenylene carbonyl), and poly(oxycarbonyl-1,4-phenylene isobutylidene-1,4-phenylene carbonyl) were synthesized with the expectation of good biodegradability. They do have good hydrolytic stability as opposed to aliphatic polyanhydrides [1]. The structures of these polymers are shown below.



In general, thermal stability of polymers from this class increases with increased aromaticity of the polymer backbone. A few reports regarding thermal stability of poly(anhydrides) include one for poly(oxycarbonyl-1,3-phenylene-hexafluoro-trimethylene-1,3-phenylene-carbonyl), which at 350° C generates a cyclic dimer [2].

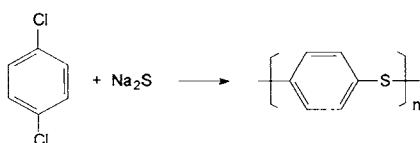
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CHAPTER 12

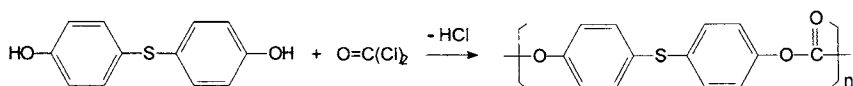
*Poly(sulfides) and Poly(sulfones)***12.1 POLY(SULFIDES)****- General aspects**

Polysulfides can be obtained from the reaction of a dihalide and Na_2S , as shown below for the formation of poly(1,4-phenylene sulfide):



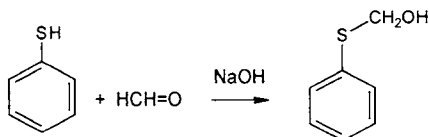
Poly(1,3-phenylene sulfide) also is known and has a decomposition temperature higher than poly(1,4-phenylene sulfide). The same reaction can take place with alkyl dihalides, such as 1,2-dichloroethane. However, since sodium sulfide is very frequently a mixture of sulfide and polysulfides, the polymer structure is better expressed by the formula $-(\text{R}-\text{S}_x-)_n$. Other reactions are known to lead to polysulfides. For example, poly(phenylene sulfide) can be obtained from 4-chlorothiophenol by self condensation in the presence of a metal base.

Some polysulfides contain in the polymer backbone other groups besides -S-. A common type of group is oxycarbonyloxy, such as in the polymer resulting from the reaction of phosgene (chloroformyl chloride or carbonic acid dichloride) with 4,4'-thiobisphenol. This reaction can be considered a polycondensation and can be written as follows:

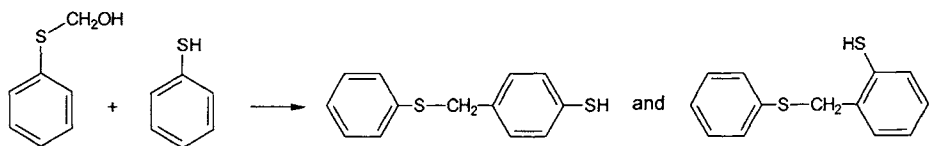


The polymer is known as poly(oxycarbonyloxy-1,4-phenylenethio-1,4-phenylene) or as poly(4,4'-dihydroxydiphenylsulfide-co-carbonic dichloride) and can be viewed as an *alt*-copolymer of a sulfide and a carbonate.

Another polymer containing sulfur in its backbone is obtained from thiophenol/formaldehyde condensation. Differently from the condensation of phenol and formaldehyde, the main reaction path for this condensation is the following:



The expected reaction with the attachment of methylol groups in *ortho* and *para* positions of the benzene ring also occur, but with much lower extent. The molecules of phenylthiomethan-1-ol continue the condensation process, forming a tridimensional resin as shown below:



Further combination of these types of reactions and also condensations similar to those encountered between phenol and formaldehyde lead to a complex tridimensional resin containing numerous C-S-C bonds [1, 2].

Poly(sulfides) have good heat resistance although the C-S bond has a dissociation energy $-\Delta H_f^\circ$ (C-S) estimated around 61 kcal/mol compared to a C-O bond with a dissociation energy $-\Delta H_f^\circ$ (C-O) estimated between 85 kcal/mol and 91 kcal/mol. The overall free enthalpy of the decomposition reaction may still be favorable, for example, to the elimination of water $\Delta H_f^\circ = -57.8$ kcal/mol as compared to the formation of H_2S with $\Delta H_f^\circ = -4.9$ kcal/mol. Also, the enthalpy of formation for phenol (in gas phase) is negative $\Delta H_f^\circ = -24.04$ kcal/mol, while that of benzenethiol (in gas phase) is $\Delta H_f^\circ = +26.86$ kcal/mol. For thermodynamic reasons, polysulfides do not decompose easily. They are used in practice as temperature resistant coatings, molding material for electrical connectors, insulating plates in electrical appliances, materials with low friction and good temperature resistance for bearings, etc.

Sulfur is part of a considerable number of polymers although not necessarily included in the polymer backbone. For example, the presence of -S-S- bridges between polymeric chains is well known for vulcanized rubber. Since the bridges are not part of the polymeric main chains, vulcanized rubber is classified together with the polymers containing double bonds in the backbone and is discussed in Section 7.2. Also sulfonic groups are present in polymers such as sulfonated styrenes (see Section 6.6) with important ion exchange properties.

Since selenium shares to a certain extent similar chemical properties with sulfur, polymers containing selenium in the backbone are conceivable. The formation and thermal properties of poly(selenoformaldehyde) have been reported in literature [3].

- Poly(phenylene sulfides)

Both poly(1,4-phenylene sulfide) ($-1,4-C_6H_4-S-$)_n CAS# 25212-74-2 and poly(1,3-phenylene sulfide) ($-1,3-C_6H_4-S-$)_n are relatively common polymers. Their thermal stability is better than that of many other polymers. Poly(1,4-phenylene sulfide) is used more frequently in practice, and several reports regarding its thermal decomposition are available. One of these reports [4] indicates that upon heating between 350° C and 450° C, the polymer starts decomposing, producing hydrogen sulfide, dimers and trimers by a radicalic mechanism. Decomposition when heated between 300° C and 620° C generates 38% residue, 47% chain fragments, and 15% volatiles comprised mainly of H₂S and H₂. The heating above 450° C leads to evolution of hydrogen and formation of radicals, which undergo cross-linking. Several other reports regarding thermal decomposition indicate that at 460° C poly(1,4-phenylene sulfide) forms H₂S, H₂, dibenzthiophene, other chain fragments, and 72% residue [5]. Another report indicates a char yield between 66% and 72% in N₂ at 800° C and between 42 and 47% in air at 800° C [6]. Heating of the polymer between 325° C and 625° C generates benzene, thiophenol, diphenyl, diphenylsulfide, dibenzothiophene, and chlorobenzene (from polymers with terminal chlorine atoms) [7]. The formation of cyclic oligomers tetramer to heptamer with the pentamer dominating [8] is reported at 560° C. Other reports on polysulfides also are available in literature [9–11].

The TGA study of a sample of poly(1,4-phenylene sulfide) is shown in Figure 12.1.1. A 4.5 mg sample was heated between 30° C and 830° C at a heating rate of 10° C/min. in air.

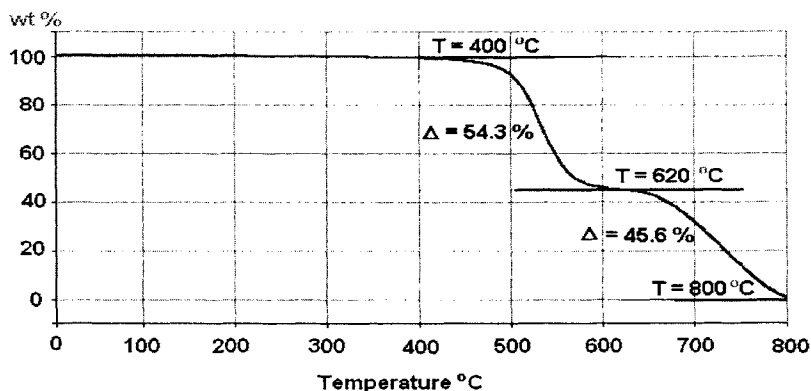


FIGURE 12.1.1. Variation of weight % loss for a poly(1,4-phenylene sulfide) sample in a TGA experiment at a heating rate of 10° C/min.

As seen from the TGA curve, the polymer starts decomposing around 450° C, and more weight loss takes place only at a heating higher than 500° C. For this reason, a Py-GC/MS experiment with the sample heated at 600° C, as performed for most polymers previously described, leads to a very weak pyrogram mainly generated from impurities, with the main peaks corresponding to the traces of water and phenol. On the other hand, the pyrogram obtained at 850° C, which is shown in Figure 12.1.2, is of higher intensity, proving the polymer decomposition. Except for the temperature, other

conditions for the Py-GC/MS experiment were similar to those used for other examples previously discussed in this book (see Table 4.2.2). The pyrolysis was performed in He at a heating rate of 20° C/ms with 10 s THT. Also, the separation was done on a Carbowax column in a GC/MS system with the mass spectrometer operating in EI+ mode. The peak identification for the chromatogram shown in Figure 12.1.2 was done using MS spectral library searches only and is given in Table 12.1.1.

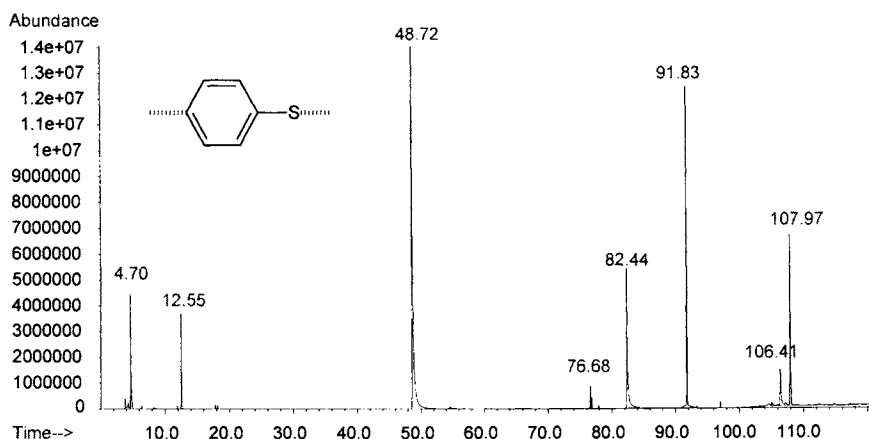


FIGURE 12.1.2. Pyrogram from a Py-GC/MS analysis of a poly(1,4-phenylene sulfide) sample. Pyrolysis done at 850° C in He, with the separation on a Carbowax type column.

TABLE 12.1.1. Compounds identified in the pyrogram of poly(1,4-phenylene sulfide) shown in Figure 12.1.2.

Peak	Compound	Ret. Time	MW	Area %
1	carbon dioxide	4.27	44	trace
2	hydrogen sulfide	4.70	34	6.24
3	1,3-cyclopentadiene	6.44	66	0.17
4	1,3-cyclohexadiene	8.31	80	trace
5	1,4-cyclohexadiene	8.56	80	trace
6	1,3-hexadien-5-yne	11.92	78	0.11
7	benzene	12.55	78	4.48
8	toluene	17.82	92	0.18
9	water	18.21	18	0.21
10	benzenethiol	48.72	110	39.29
11	biphenyl	76.68	154	1.58
12	phenol	76.85	94	trace
13	1,4-benzendithiol	82.44	142	12.78
14	diphenyl sulfide	91.83	186	18.68
15	2-methyl-5-styrylthiophene	97.06	200	0.35
16	4-phenylbenzene-1-thiol ?	106.41	186	3.63
17	dibenzothiophene	107.97	184	12.30

The cleavage of the polymeric backbone takes place at the S-C_(aromatic) bond with the formation of a thiol group. As reported in literature [4], the mechanism is probably

radical and associated with formation of some biphenyl fragments. Since the experimental conditions for generating the pyrogram in Figure 12.1.2 allow only the detection of the volatile pyrolysis products, larger fragments formed during the pyrolysis were not analyzed. Among the pyrolysis products was tentatively identified 4-phenylbenzene-1-thiol (retention time 106.41 min.), which does not have a mass spectrum available in the commercial mass spectral libraries. Its spectrum is shown in Figure 12.1.3.

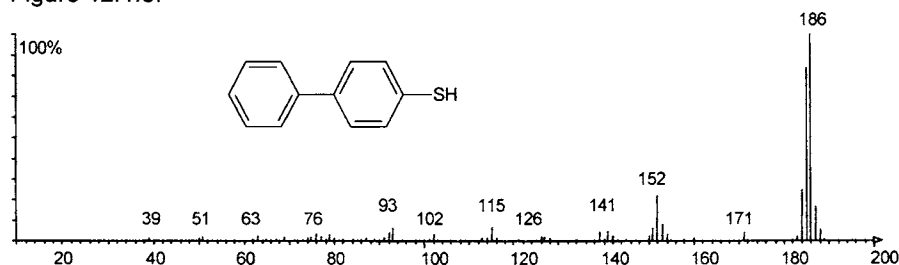


FIGURE 12.1.3. Mass spectrum tentatively identified as generated by 4-phenylbenzene-1-thiol eluting at 106.41 min. in the pyrogram shown in Figure 12.1.2.

The spectrum of 4-phenylbenzene-1-thiol is almost identical to that of diphenyl sulfide (retention time 91.83 min.), which has the spectrum shown in Figure 12.1.4 and is available in commercial mass spectral libraries.

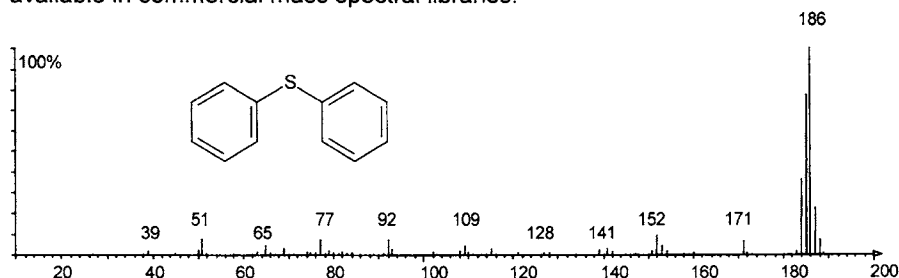


FIGURE 12.1.4. Mass spectrum of diphenyl sulfide.

The spectrum of 4-phenylbenzene-1-thiol has clear similarities with that of benzenethiol (from common mass spectral libraries), which is shown in Figure 12.1.5.

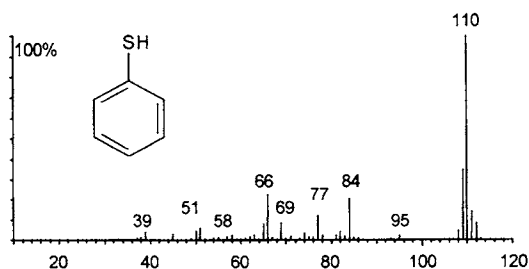


FIGURE 12.1.5. Mass spectrum of benzenethiol.

Fewer studies are dedicated to the thermal decomposition of poly(1,3-phenylene sulfide). One such study [8] indicates the formation of a cyclic dimer (thianthrene) and some cyclic trimer. The same behavior is confirmed for the decomposition at 530° C when the polymer forms cyclic oligomers (trimer to heptamer in decreasing yield) [8].

- Other polysulfides

Reports on the thermal decomposition for several other polysulfides are available in literature. A summary of such reports is given in Table 12.1.2.

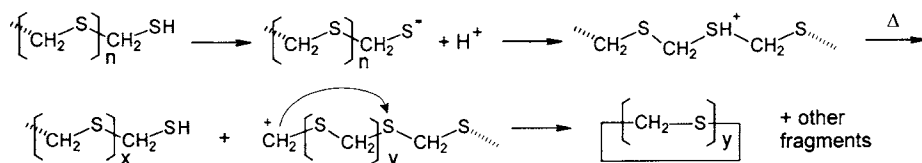
TABLE 12.1.2. *Summary regarding literature studies on thermal decomposition of several polysulfides [12].*

Polymer	Temp. °C	Results	Ref.
poly(thioacetone)	145	main product is cyclic trimer [(CH ₃) ₂ CS]	13
poly(thioethylene)	220–260	ethylene, H ₂ S, ethanethiol	14
poly(thio-1,4-perfluorophenylene)	500	73% residue; remainder, chain fragments, H ₂ , SiF ₄ (from silica vessel), CO ₂	5
poly(thiomethylene-1,4-phenylene-methylene)	250–350	sulfur, styrene, thiobenzaldehyde, 4-methylstyrene, p-xylene, 4-ethyltoluene, H ₂ S, 4-methylthiobenzaldehyde, stilbene and chain fragments containing stilbene units, chain fragments containing polymer repeat units with -CH ₂ SH, -CH=S and -CH ₃ terminal units	15
poly(thiomethylene-1,4-phenylene-methylene)	650	toluene, ethylbenzene, p-xylene, 1,4-diethylbenzene, 4-ethyltoluene; series of polycyclic aromatics containing phenanthrene and dihydrophenanthrene	15
poly(dithiomethylene-1,4-phenylene-methylene)	250–350	sulfur, styrene, thiobenzaldehyde, 4-methylstyrene, p-xylene, 4-ethyltoluene, H ₂ S, 4-methylthiobenzaldehyde, stilbene and chain fragments containing stilbene units, chain fragments containing polymer repeat units with -CH ₂ SH, -CH=S and -CH ₃ terminal units	15
poly(dithio-methylene-1,4-phenylene-methylene)	650	toluene, ethylbenzene, p-xylene, 1,4-diethylbenzene, 4-ethyltoluene; series of polycyclic aromatics containing phenanthrene and dihydrophenanthrene	15
thiophenol/formaldehyde resin	350, 475, 575	toluene, thiophenol, benzyl mercaptan, methylthiobenzene, benzothiophene, methylbenzothiophene, diphenylmethane, diphenyl sulfide, methylphenyl phenyl sulfide, benzyl phenyl sulfide, dibenzothiophene, thioxantene, diphenyl disulfide, thianthrene, p-mercaptobenzyl phenyl sulfide, biphenyl, bibenzyl, stilbene, thiobenzophenone, diphenylmethanethiol, triphenylethylene	2

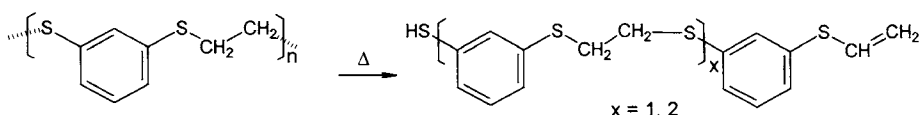
The information from Table 12.1.2 mainly refers to thermal decomposition in conditions different from those used in flash pyrolysis. However, the nature of pyrolysis products during flash pyrolysis is not usually very different from that resulting from thermal decomposition at slower rates but at similar temperatures. Also, the decomposition mechanisms are similar, and cleavages occur at the weaker bonds in the polymer. For example, for thiophenol/formaldehyde resin the benzylic C–S bond is the weakest in the resin, and its cleavage is the key step in the formation of most pyrolysis products.

Other reports on polysulfide thermal decomposition include a study on pyrolysis mass spectrometry at low temperatures between 240 and 350° C of polythiomethylene (in the presence of ammonium polyphosphate), polythioethylene, and poly(3-vinylthiobenzene-1-thiol) [16]. This study shows that the formation of cyclic oligomers is the main process

that occurs during the pyrolysis of these compounds. The process can be described schematically for polythiomethylene by the following sequence of reactions:



This reaction scheme can explain, for example, the formation of 1,3,5-trithiane, which is one of the main components in the pyrolysis products of polythiomethylene. In a similar reaction, polythioethylene generates 1,4-dithiane, but the formation of cyclic fragments from poly(3-vinylthiobenzene-1-thiol) is less favored and the decomposition occurs mainly as indicated below:



Thermal decomposition of a polymer with the structure $\text{HS}-(\text{R}-\text{S}-\text{S})_n-\text{R}-\text{SH}$ with $\text{R} = -(\text{CH}_2)_2-\text{O}-\text{CH}_2-\text{O}-(\text{CH}_2)_2-$ cured with various oxidizing agents such as ammonium dichromate also has been reported [17]. Flash pyrolysis was performed at 420°C and 470°C generating a mixture of compounds where 1,3-oxathiolane, 2-mercaptomethyloxirane, 1,3-dioxo-6-thiocane and 1,3-dioxo-6,7-dithionane were the main components.

References 12.1

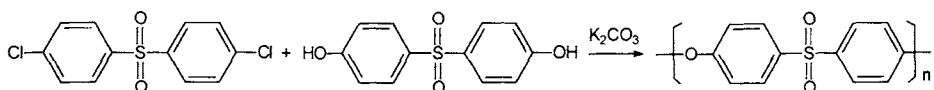
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12.2 POLY(SULFONES)

- General aspects

A free radical polymerization reaction in the presence of a peroxide or hydroperoxide can take place between an olefin and SO_2 . The resulting poly(olefin sulfone) may have a variable composition (variable content of SO_2), but poly(ethylene-*alt*-sulfur dioxide), CAS# 110711-58-5, or poly(ethylene sulfone) can be obtained. Different olefins can be used in the reaction, as well as butadiene. Poly(sulfur dioxide-co-alkenes) may have a variable composition from 1:1 mole ratio (*alt* copolymer) to various other monomer ratios.

Other poly(sulfones) can be obtained similarly to poly(sulfides) by polycondensation. Many of these sulfones also contain an ether group in the backbone. A typical reaction for the formation of a poly(ether sulfone) is that of 4,4'-dichlorodiphenylsulfone with 4,4'-sulfonyldiphenol or bisphenol S in the presence of K_2CO_3 (as a base) as shown below:



The resulting poly(oxy-1,4-phenylene sulfonyl-1,4-phenylene) (PES), CAS# 25667-42-9, is a valuable polymer used to make various household appliances, medical devices, automotive parts, etc. The polymer can be shaped by thermoforming and is used in various composite materials. It has good fire safety characteristics and meets the requirements for direct food contact. Other polyethersulfones with structures similar to PES also have important practical applications and are used for the manufacturing of different appliances, cookware, automotive and aerospace components, etc.

- Poly(alkene sulfones) and their copolymers

A number of poly(alkene sulfones) or poly(sulfur dioxide-co-alkenes) can be synthesized by free radical reaction between an olefin or a diene and sulfur dioxide. The initiation can be done with oxygen, peroxides, hydroperoxides, at high pressure and elevated temperatures. Among the compounds obtained in this way are the following copolymers: ethene/ SO_2 CAS# 28085-22-5, 1-butene/ SO_2 CAS# 25104-10-3, *E*-2-butene/ SO_2 CAS# 34903-09-8, *Z*-2-butene/ SO_2 CAS# 34903-08-7, 2-methyl-1-propene/ SO_2 CAS# 29436-19-9, 2-pentene/ SO_2 CAS# 64155-67-5, 1-hexene/ SO_2 CAS# 34903-07-6, and several other compounds from this class with longer carbon chains such as 1-octadecene/ SO_2 copolymer CAS# 33991-02-5. Since poly(alkene sulfones) are very sensitive to ionizing radiation and undergo a rapid chain scission with the cleavage occurring predominantly at the C-S bond, these compounds have special practical applications in photolithography. Some poly(alkene sulfones) are used in antistatic formulations.

Thermal decomposition of 1-alkene polysulfones yields mainly the respective monomers. Cyclic alkene sulfones and 2-alkene sulfones undergo a more complex

decomposition yielding a variety of products including aromatics [1]. Ethylene polysulfone is stable up to about 225° C. Above 275° C decomposition proceeds rapidly, with 100% weight loss around 350° C. A copolymer with only 9 mol% SO₂ decomposes more slowly than the *alt*-copolymer. The polysulfones of norbornene and some of its derivatives are thermally more stable than those of 1-butene and cyclohexene. Stability can be enhanced by the use of stabilizers such as thioacetamide or tin(II) oxide. A summary of some reports on the thermal decomposition for several poly(alkene sulfones) given in literature is shown in Table 12.2.1.

TABLE 12.2.1. Summary regarding literature studies on thermal decomposition of several poly(sulfur dioxide-co-alkenes) [2].

Polymer	Temp. °C	Results	Ref.
poly(sulfur dioxide-co-1-butene)	700-800	monomers	3
poly(sulfur dioxide-co-1-butene)	190	monomers, weight loss 30.5% after 3 hours	2
poly(sulfur dioxide-co-1-hexene)	700-800	monomers	3
poly(sulfur dioxide-co-1-octadecene)	700-800	monomers	3
poly(sulfur dioxide-co-5-norbornene-2-carbonitrile)	190	weight loss 5.4% after 3 hours	2
poly(sulfur dioxide-co-bicycloheptene)	700-800	SO ₂ , bicycloheptene, cyclopentadiene, ethylene, methylcyclohexadiene, benzene, indene, naphthalene, dihydronaphthalenes	3
poly(sulfur dioxide-co-cis-2-butene)	700-800	SO ₂ , butenes, benzene, toluene, octadienes, xylenes, styrene, indene, naphthalene	3
poly(sulfur dioxide-co-cyclohexene)	190	SO ₂ , cyclohexene, weight loss 16.1% after 3 hours	2
poly(sulfur dioxide-co-cyclopentene)	700-800	SO ₂ , cyclopentene, xylenes, ethylbenzene, styrene, indene, decadienes, dihydronaphthalenes, tetralin, naphthalene	3
poly(sulfur dioxide-co-methyl methacrylate-co-1-hexene) 24.1/1	700-800	SO ₂ , hexenes, hexadienes, methyl methacrylate, toluene, naphthalene, dodecadienes	3
poly(sulfur dioxide-co-methyl methacrylate-co-bicycloheptene)	700-800	SO ₂ , ethylene cyclopentadiene, benzene, methyl methacrylate, bicycloheptene, methylcyclohexa-2,4-diene, ethylbenzene, xylenes, styrene, indene, naphthalene, dihydronaphthalenes	3

As seen from Table 12.2.1, SO₂ and the hydrocarbon type monomer are the main thermal decomposition products of all the listed compounds. The decomposition reaction seems to occur by the following scheme:



Results for a Py-GC/MS analysis of poly(1-hexene-sulfone) CAS# 34903-07-6 with the idealized structure $[-CH(C_4H_9)-CH_2-SO_2-CH_2-CH(C_4H_9)-SO_2-]_n$ are shown in Figure 12.2.1. The pyrolysis was done in similar conditions as for other examples, at 600° C in

He at a heating rate of 20° C/ms. with 10 s THT. The separation was done on a Carbowax column with the GC starting at 40° C with a ramp of 2° C/min. up to 240° C and a final oven time of 20 min. (see Table 4.2.2). The peak identification for the pyrogram was done using mass spectral library searches only and is given in Table 12.2.2.

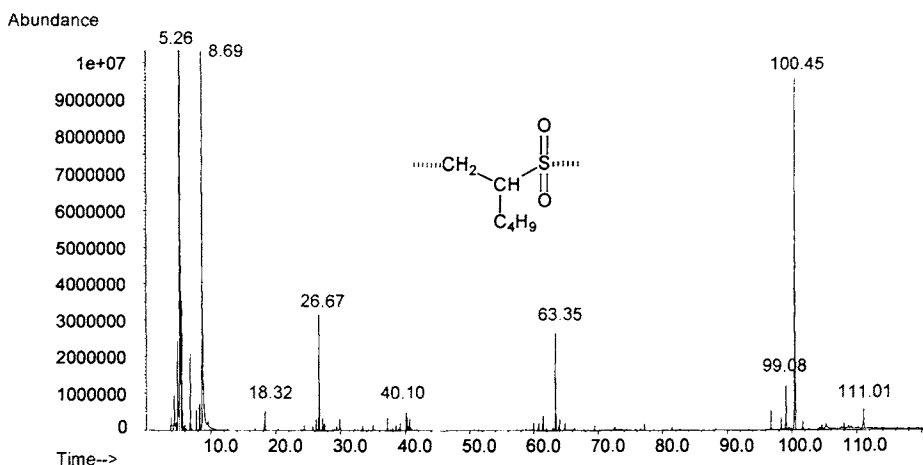


FIGURE 12.2.1. Result for a Py-GC/MS analysis of poly(1-hexene sulfone). Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 12.2.2. Compounds identified in the pyrogram of poly(1-hexene sulfone) as shown in Figure 12.2.1.

Peak	Compound	Ret. Time	MW	Area %
1	propene	4.37	42	1.40
2	2-methylpropene	4.45	56	trace
3	hydrogen sulfide	4.67	34	0.11
4	2-methylpentene	4.92	84	3.07
5	1-hexene	5.26	84	36.56
6	2-hexene	5.38	84	trace
7	3-hexene	5.53	84	trace
8	<i>trans</i> -1,4-hexadiene	5.97	82	0.20
9	<i>cis</i> -1,3-hexadiene	6.83	82	1.59
10	(<i>Z,Z</i>)-2,4-hexadiene	7.74	82	0.39
11	(<i>E,E</i>)-2,4-hexadiene	8.25	82	0.58
12	sulfur dioxide	8.69	64	24.12
13	thiophene	16.76	84	trace
14	water	18.32	18	0.87
15	hexanal	20.42	100	trace
16	1-hexanethiol	24.43	118	0.14
17	2,5-dimethylthiophene	25.72	112	0.12
18	1,1,3,5-tetramethylcyclohexane ?	26.26	140	0.30
19	3-ethylthiophene	26.67	112	3.63
20	hydrocarbon ?	27.25		0.33
21	cyclohexanethiol ?	27.53	116	0.21
22	3-[(1-methylethyl)thio]-1-propene ?	29.40	116	0.13

TABLE 12.2.2 (continued). *Compounds identified in the pyrogram of poly(1-hexene sulfone) as shown in Figure 12.2.1.*

Peak	Compound	Ret. Time	MW	Area %
23	3-dodecene	29.84	168	0.50
24	2-ethylthiophene	33.43	112	0.19
25	unknown [81(100), 109(45), 166(40), 95(38), 67(24), 137(16)]	37.23	166	0.47
26	unknown [81(100), 166(44), 95(37), 109(32), 67(25)]	38.57	166	0.17
27	5,7-dodecadiene ?	39.20	166	0.26
28	C ₁₂ H ₂₂ ?	40.10	166	0.96
29	C ₁₂ H ₂₂ ?	40.69	166	0.33
30	2,5-dibutylthiophene	59.95	196	0.26
31	unknown substituted thiophene [125(100), 139(69), 154(57), 196(48), 111(28)]	60.73		0.33
32	unknown [154(100), 153(50), 111(42), 196(29), 112(20)]	61.40		0.47
33	unknown substituted thiophene [111(100), 139(55), 154(45), 196(34), 126(18)]	63.35	196	3.09
34	dicyclohexylsulfide	63.98	198	0.43
35	unknown [198(100), 85(67), 155(39), 83(39), 41(39)]	64.80		0.24
36	mix	96.76		0.56
37	unknown [55(100), 82(68), 83(60), 41(45), 149(41), 67(21)]	98.30		0.40
38	unknown [55(100), 83(85), 82(63), 41(46), 149(32), 67(20)]	99.08		1.49
39	(hexylsulfonyl)[5-methyl(2-thienyl)]methane ?	100.45	260	14.35
40	unknown	105.26		0.72
41	unknown [55(100), 189(90), 175(83), 41(83), 81(77), 67(65)]	111.01		1.03

As seen from Table 12.2.2, the main pyrolysis products of poly(1-hexene-sulfone) are SO₂ and 1-hexene. However, some other fragment molecules are generated by various types of reactions such as hydrogen transfer, cyclization, etc. Typical examples are 2-ethylthiophene, 3-ethylthiophene, and 2,5-dibutylthiophene.

- Poly(ether sulfones)

The class of poly(ether sulfones) includes a number of compounds obtained by polycondensations similar to that between bisphenol A and 4,4'-dichlorodiphenylsulfone, which generates PES. Among more common poly(ether sulfones) are poly[oxy(1,1'-biphenyl)-4,4'-diyoxy-1,4-phenylene-sulfonyl-1,4-phenylene] (PPSF) CAS# 25608-64-4, which is synthesized from the reaction of 4,4'-dichlorodiphenyl-sulfone with 1,1'-biphenyl-4,4'-diol in the presence of a base, and poly[oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylene(1-methylethylidene)-1,4-phenylene] (PSF) CAS# 25135-51-7, which is obtained from bisphenol A and 4,4'-dichlorodiphenylsulfone.

Poly(ether sulfones) containing aromatic rings in the backbone have much better thermal stability compared to poly(sulfur dioxide-co-alkenes). For example, PSF degrades very slowly in vacuum above 400° C, and only above 460° a more rapid decomposition begins [4]. Other poly(ether sulfones) behave similarly [5]. Several reports on the thermal decomposition for poly(ether sulfones) are available in literature. A summary of such reports are given in Table 12.2.3.

TABLE 12.2.3. Summary regarding literature studies on thermal decomposition of several poly(ether sulfones) [2].

Polymer	Temp. °C	Results	Ref.
poly(oxy-1,4-phenylene-sulfonyl-1,4-phenylene)	470 for 2 h	phenol (main product), diphenyl oxide	6
poly(oxy-1,4-phenylene-sulfonyl-1,4-phenylene)	550–600	SO ₂ , diphenylsulfone, phenol, diphenylether, hydroquinone, benzenesulfonic acid, 4-hydroxybenzenesulfonic acid, 4,4'-dihydroxydiphenyl ether, 4-phenoxyphenol; series of -H and -OH terminated fragments up to trimer, series of compounds containing consecutive diphenyl ether and dibenzofuran units, fragments containing biphenyl units as a result of SO ₂ elimination, complex ring structures with sulfonate links	7
poly(oxy-1,4-phenylene-sulfonyl-1,4-phenylene)	800	SO ₂ , benzene, phenol, diphenyl ether, dibenzofuran	8
poly(oxy-1,4-phenylene-sulfonyl-1,4-phenylene-oxy-1,4-phenylene-isopropylidene-1,4-phenylene)	380	phenol with smaller amounts of p-cresol, p-ethyl phenol, p-isopropylphenylphenol, bisphenol A, diphenyl ether, p-tolyl phenyl ether, p-ethyl diphenyl ether, p-isopropenyl diphenyl ether, isomers of tolyl (ethyl-phenyl) ether	9
poly(oxy-1,4-phenylene-sulfonyl-1,4-phenylene-oxy-1,4-phenylene-isopropylidene-1,4-phenylene)	350–450	90 min. at 450° C, 15% (of initial weight) of gaseous products are formed; SO ₂ (76% of gaseous products), CO ₂ (15%), CO (4.5%), CH ₄ (4.5%)	10
poly(oxy-1,4-phenylene-sulfonyl-1,4-phenylene-oxy-1,4-phenylene-isopropylidene-1,4-phenylene)	470 for 2 h	benzene, toluene, p-xylene, isopropylbenzene, phenol (main product), diphenyl oxide, diphenyl sulfide	6
poly(oxy-1,4-phenylene-sulfonyl-1,4-phenylene-oxy-1,4-phenylene-isopropylidene-1,4-phenylene)	800	SO ₂ , benzene, toluene, styrene, phenol, methylphenol, diphenyl ether, methyl diphenyl ether	8
poly(oxy-1,4-phenylene-sulfonyl-1,4-phenylene-oxy-1,4-phenylenemethylene-1,4-phenylene)	unspec.	benzene, toluene, p-xylene, phenol (main product), diphenyl oxide	6
poly(oxy-4,4'-diphenylene-oxy-1,4-phenylene-sulfonyl-1,4-phenylene)	unspec.	phenol (main product), diphenyl oxide	6
poly(tris-(oxy-1,4-phenylene)sulfonyl-1,4-phenylene)	unspec.	benzene, phenol (major product), diphenyl oxide, p-hydroxydiphenyl, or p-hydroxydiphenyl oxide	6

Results for a Py-GC/MS analysis of poly(oxy-1,4-phenylenesulfonyl-1,4-phenylene) or poly(1,4-phenylene ether sulfone) or PES CAS# 25667-42-9, with the idealized structure $(-\text{OC}_6\text{H}_4-\text{SO}_2-\text{C}_6\text{H}_4-)_n$, are shown in Figure 12.2.2. Either because the mass of the pyrolysis tube holding the sample in the typical experimental setup (on a CDC Pyroprobe 2000) is too large for attaining rapidly enough the equilibrium temperature, or because the polymer decomposes slowly at 600° C, it was found that pyrolysis of PES at 600° C does not give a diagnostic pyrogram. Only traces of phenol are clearly detected at that temperature. For this reason, it was necessary to perform this pyrolysis at the increased temperature. The pyrolysis was done at 850° C in He at a heating rate of 20° C/ms. with 10 s THT. The separation was done in similar conditions to other experiments previously described (see Table 4.2.2), on a Carbowax column with the GC starting at 40° C with a ramp of 2° C/min. up to 240° C and a final oven time of 20 min. The peak identification for the pyrogram was done using mass spectral library searches only and is given in Table 12.2.4.

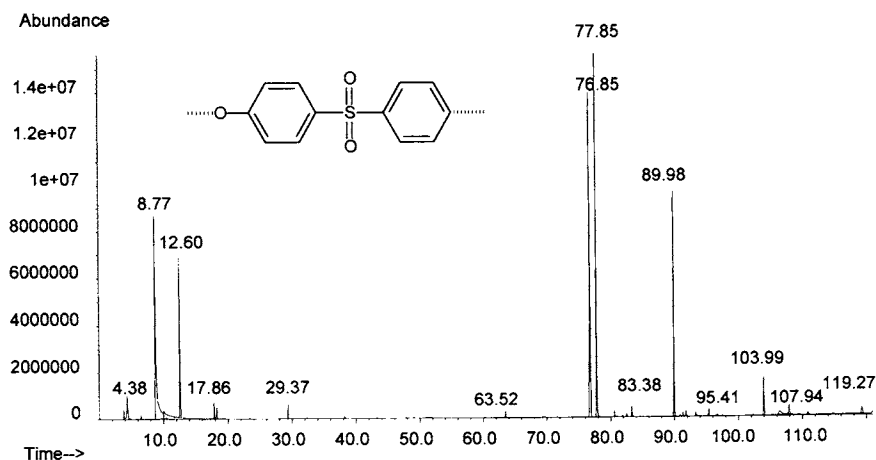


FIGURE 12.2.2. Result for a Py-GC/MS analysis of poly(oxy-1,4-phenylenesulfonyl-1,4-phenylene). Pyrolysis done on 0.4 mg material at 850° C in He, with the separation on a Carbowax type column.

TABLE 12.2.4. Compounds identified in the pyrogram of poly(oxy-1,4-phenylene-sulfonyl-1,4-phenylene) as shown in Figure 12.2.2.

Peak	Compound	Ret. Time	MW	Area %
1	carbon monoxide	4.38	28	2.34
2	1,3-cyclopentadiene	6.50	68	trace
3	sulfur dioxide	8.77	64	19.94
4	benzene	12.60	78	7.64
5	toluene	17.86	92	0.73
6	water	18.31	18	0.84
7	ethylbenzene	23.38	106	trace
8	chlorobenzene (resulting from synthesis reagents)	29.37	112	0.65
9	styrene	32.31	104	trace
10	methoxybenzene	38.20	108	trace
11	1H-indene	47.90	116	trace
12	benzofuran	49.10	118	trace
13	thiophenol	51.40	110	trace
14	3-methylbenzofuran	54.73	132	trace
15	naphthalene	63.52	128	0.34
16	benzo[b]thiophene	67.15	134	trace
17	1-methylnaphthalene	69.32	142	trace
18	1,1'-biphenyl	76.67	154	4.03
19	phenol	76.85	94	26.27
20	1,1'-oxy-bisbenzene	77.85	170	19.89
21	4-methylphenol	80.64	108	0.33
22	3-methylphenol	81.02	108	trace
23	4-methyl-1,1'-biphenyl	81.86	168	trace
24	3-methyl-1,1'-biphenyl	83.53	168	trace
25	1-methyl-4-phenoxybenzene	83.38	184	0.53
26	dibenzofuran	89.98	168	12.13
27	1-chloro-4-phenoxybenzene (impurity)	91.36	204	0.24

TABLE 12.2.4 (continued). Compounds identified in the pyrogram of poly(oxy-1,4-phenylene-sulfonyl-1,4-phenylene) as shown in Figure 12.2.2.

Peak	Compound	Ret. Time	MW	Area %
28	diphenylsulfide	91.83	186	0.33
29	fluorene	93.33	166	trace
30	9H-xanthene	95.18	182	trace
31	4-methyldibenzofuran	95.41	182	0.48
32	4-hydroxybiphenyl	103.99	170	1.95
33	dibenzothiophene	107.94	184	0.72
34	anthracene	110.60	178	trace
35	2-phenoxy-1,1'-biphenyl	119.27	246	0.61

Results for a Py-GC/MS analysis of polysulfone or bisphenol A polyethersulfone or PSF CAS# 25135-51-7, with the formula $[-C_6H_4-4-C(CH_3)_2-C_6H_4-4-O-C_6H_4-4-SO_2-C_6H_4-4-O-]_n$ $M_w = 67,000$, are shown in Figure 12.2.3. The pyrolysis was done at 850° C in He since this polymer is also resistant to thermal decomposition. Other experimental conditions for pyrolysis and for the analysis of the pyrolysate were maintained the same as for other examples discussed in this book (see Table 4.2.2). The peak identification for the pyrogram was done using mass spectral library searches only and is given in Table 12.2.5.

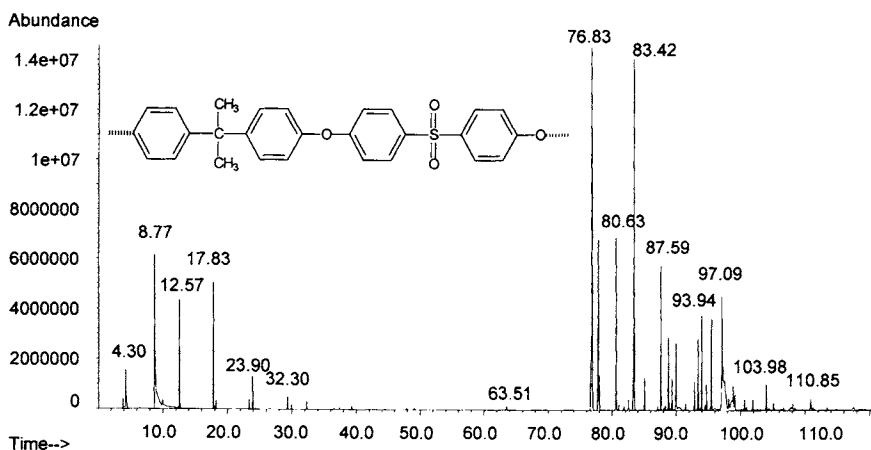


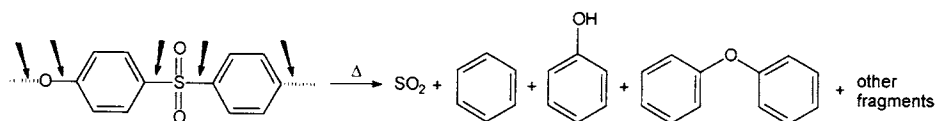
FIGURE 12.2.3. Result for a Py-GC/MS analysis of bisphenol A polyethersulfone (PSF). Pyrolysis done on 0.4 mg material at 850° C in He, with the separation on a Carbowax type column.

TABLE 12.2.5. Compounds identified in the pyrogram of bisphenol A polyethersulfone as shown in Figure 12.2.3.

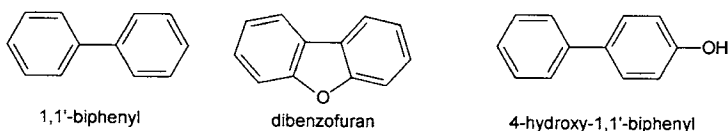
Peak	Compound	Ret. Time	MW	Area
1	methane	4.30	16	1.68
2	carbon monoxide	4.38	28	trace
3	1,3-cyclopentadiene	6.50	68	trace
4	sulfur dioxide	8.77	64	8.37
5	benzene	12.57	78	3.64
6	toluene	17.84	92	3.69
7	water	18.26	18	0.37
8	ethylbenzene	23.38	106	0.25
9	1,4-dimethylbenzene	23.90	106	0.87
10	chlorobenzene (impurity)	29.34	112	0.38
11	1-ethyl-2-methylbenzene	29.95	120	trace
12	styrene	32.31	104	0.21
13	α -methylstyrene	37.42	118	trace
14	1-ethenyl-4-methylbenzene	39.30	118	trace
15	1H-indene	47.90	116	trace
16	benzofuran	49.10	118	trace
17	thiophenol	51.40	110	trace
18	naphthalene	63.52	128	trace
19	1-methylnaphthalene	69.32	142	trace
20	1,1'-biphenyl	76.67	154	trace
21	phenol	76.83	94	18.58
22	1,1'-oxy-bisbenzene	77.82	170	6.24
23	diphenylmethane	78.00	168	trace
24	4-methylphenol	80.63	108	5.56
25	3-methylphenol	81.02	108	0.16
26	3-methyl-1,1'-biphenyl	82.54	168	0.43
27	1-methyl-4-phenoxybenzene	83.42	184	13.07
28	4-ethylphenol	85.04	122	0.94
29	4-ethylphenoxybenzene	87.59	198	4.45
30	1,1'-oxybis(4-methylbenzene)	88.79	198	2.17
31	phenyl <i>p</i> -isopropylphenyl ether	89.32	212	1.03
32	dibenzofuran	89.96	168	2.14
33	phenyl <i>p</i> -propylphenyl ether	91.42	212	0.20
34	phenyl <i>m</i> -isopropylphenyl ether	92.80	212	0.93
35	fluorene	93.36	166	2.36
36	phenyl (3-vinylphenyl) ether	93.94	196	2.92
37	4-methylbenzaldehyde	94.68	120	0.79
38	4-methyldibenzofuran	95.41	182	3.11
39	2,3-dihydro-2-methyl-4-phenylbenzofuran	97.09	210	9.88
40	mix with 3-hydroxybiphenyl	97.23	170	trace
41	2-methyl-9H-fluorene	98.17	180	0.49
42	1-methoxy-2-(2-phenylethenyl)benzene	98.84	210	2.09
43	4(1-methylethyl)-1,1'-biphenyl	99.11	196	0.60
44	4-(2-phenylethyl)phenol ?	100.60	196	0.39
45	4-hydroxybiphenyl	103.98	170	0.88
46	2-hydroxybenz[a]naphthalene	105.12	194	0.33
47	7-ethyl-1,4-dimethylazulene ?	108.10	184	0.27
48	phenanthrene	110.85	178	0.53

The fragmentation of both polymers PES and PSF at 850° C takes place at various non-aromatic bonds in the molecule. Several fragment molecules formed at higher level

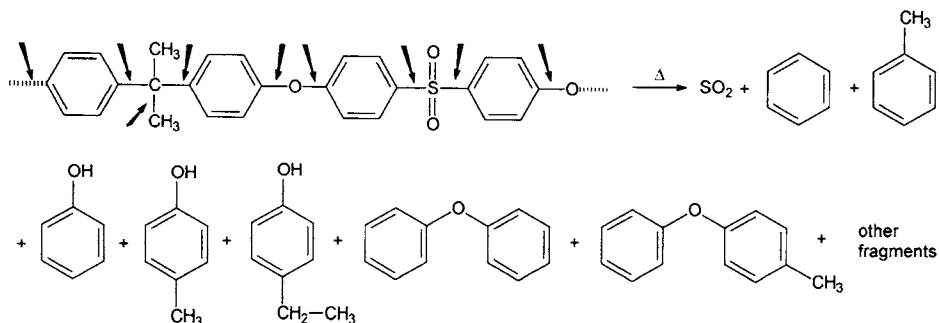
directly from fragmentation of poly(1,4-phenylene ether sulfone) or PES are indicated below [9]:



Diphenylsulfone was not detected in the pyrolysate, either because it is not formed at detectable levels, or because it may not elute from the Carbowax column used for the separation of the pyrolysate. However, this compound and other sulfur-containing compounds may be formed during pyrolysis and not detected in the analysis step. The SO_2 group represents 27.58% of the weight of the polymer, and only 19.94% molecular SO_2 is detected in the pyrogram (assuming equal detector response for all analytes). The other sulfur-containing compounds except for diphenylsulfide (0.33%) and dibenzothiophene (0.72%) are at a trace levels. The thermal decomposition of PES takes place, very likely, by a radicalic mechanism, and the free radicals can interact and form other stable molecules such as biphenyl (~4 % of volatile pyrolysate), 4-hydroxybiphenyl (~2% of volatile pyrolysate) and dibenzofuran (~12% of volatile pyrolysate) which are shown below:



The fragmentation during pyrolysis of bisphenol A polyethersulfone (PSF) is analogous to that of PES and is indicated schematically below:

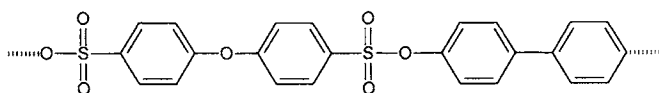


Very likely, only part of the bisphenol A is decomposed during pyrolysis, and the compound is probably present in the pyrolysate. However, bisphenol A (which has the base peak at 213 a.u. and the molecular ion at 228 a.u.) was not detected in the pyrogram. Bisphenol A does not elute in the experimental conditions used for the pyrolysate separation.

Similarly to the case of PES, pyrolysis of bisphenol A polyethersulfone (PES) is very likely radicalic, and the compounds generated by the termination reaction with reaction of two free radicals include dibenzofuran, 4-methyl-dibenzofuran, etc. Also during pyrolysis of PSF it is possible that diphenylsulfone and other sulfur-containing compounds are formed but are not detected in the analysis step. The SO₂ group represents 14.48% of the weight of PSF, and only 8.37% molecular SO₂ is detected in the pyrogram shown in Figure 12.2.3.

Pyrolysis in the presence of tetramethylammonium hydroxide (TMAH) at a lower temperature of 300° C was studied for both PES and PSF [11]. In this study, the main component for the thermally assisted hydrolysis and methylation of PES was dimethyl derivative of bis(4-hydroxyphenyl)sulfone. This compound was formed through selective cleavages of ether linkages maintaining intact the sulfone structures. For PSF thermally assisted hydrolysis and methylation at 300° C, the main constituents were dimethyl derivative of bis(4-hydroxyphenyl)isopropylidene (bisphenol A) and also dimethyl derivative of bis(4-hydroxyphenyl)sulfone. A partial decomposition of the sulfone groups in PSF during the THM reaction also was noted. The findings also were confirmed by matrix assisted laser desorption mass spectrometric measurements.

Besides polysulfones, syntheses of polysulfonates also are known. For example, the condensation of diphenylether-4,4'-disulphonyl chloride and 4,4'-dihydroxydiphenyl generates the polymer with the following structure:



This polymer decomposes at relatively low temperatures (less than 300° C) with formation of SO₂ and various molecular fragments [12].

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CHAPTER 13

Poly(imines), Urea Thermosetting Resins, Poly(amides), and Poly(imides)

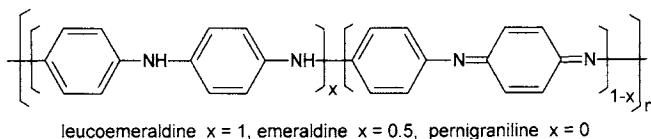
13.1 POLY(IMINES)

- General aspects

Poly(imines) are polymers that contain in their backbone amino nitrogens connected by single bonds to carbon atoms. Some of these polymers have a simple structure like poly(ethylene imine) or $[-CH_2-CH_2-NH-]_n$. The polymer is obtained from the polymerization of aziridine, typically generating a mix of linear and branched macromolecules with about 25% primary amine groups, 50% secondary amine groups, and 25% tertiary amine groups. The polymer is used in paper industry and for various other purposes that make use of its anionic character [1].

The poly(imine) dendrimers form a special type of polymer. The dendrimers have different physical properties from linear polymers, and some have been used for biomedical applications. Dendrimers typically start with a core molecule. Ammonia can be used for this purpose. In the presence of methanol, ammonia reacts with methyl acrylate forming $N(CH_2CH_2COOCH_3)_3$. The resulting molecule can react further with ethylenediamine or other diamines forming $N(CH_2CH_2CONHCH_2CH_2NH_2)_3$. At the end of each branch is a free amino group that can react with two methyl acrylate monomers and further with two ethylenediamine molecules. The continuation of the process leads to a dendrimer (polyamidoamine or PAMAM) [2]. A different dendrimer is poly(propylene imine), which has butylenediamine as a core molecule.

Another polymer with special properties from the class of polyimines is polyaniline, which can be obtained in a form with good electrical conductivity [3]. The idealized formula of polyaniline (for the nonionized form) is shown below:



The polymer is used in microwave absorbers and as conductive coating with good abrasion resistance for electronic components. Polyaniline is not thermoplastic and cannot be melted or even softened by heat. It is still stable up to about 240° C and starts decomposing at higher temperatures.

A similar polymer to poly(aniline) is poly(*o*-toluidine). The polymer can be synthesized electrochemically, and it is typically doped for modifying its electrical properties. Common dopants are salicylidine-aniline and salicylidine-*o*-aminophenol. Reports on thermal stability of this polymer are available in literature [4].

Results for a Py-GC/MS analysis of a poly(ethylene imine) sample (mix of linear and branched chains), CAS# 29320-38-5, with $M_n = 423$, are shown in Figure 13.1.1. The pyrolysis was done in similar conditions as for other examples previously discussed in this book, at 600° C in He at a heating rate of 20° C/ms. with 10 s THT. The separation was done on a Carbowax column with the GC starting at 40° C with a ramp of 2° C/min. up to 240° C and a final oven time of 20 min. (see Table 4.2.2). The peak identification for the chromatograms shown in Figure 13.1.1 was done using MS spectral library searches only and is given in Table 13.1.1.

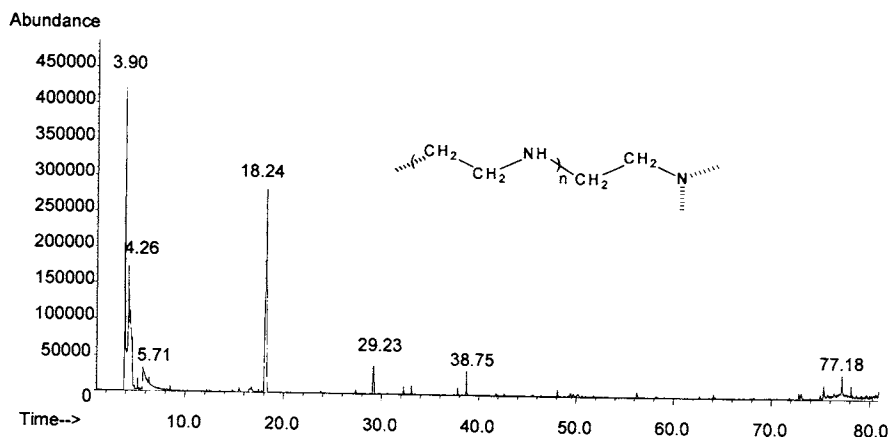


FIGURE 13.1.1. Result for a Py-GC/MS analysis of a poly(ethylene imine) sample (mix of linear and branched chains) with $M_n = 423$. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

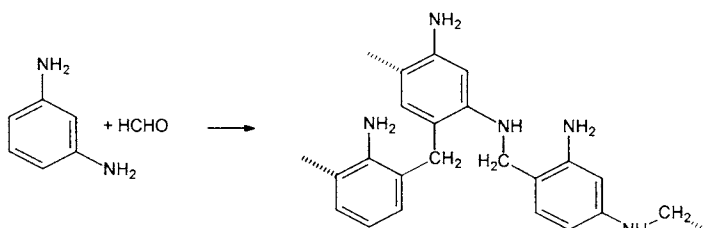
TABLE 13.1.1. Compounds identified in the pyrogram of a poly(ethylene imine) sample (mix of linear and branched chains) with $M_n = 423$ as shown in Figure 13.1.1.

Peak	Compound	Ret. time	MW	Area %
1	air (contaminant)	3.90		not counted
2	ethene	4.26	28	49.50
3	carbon dioxide (contaminant)	4.41	44	not counted
4	ammonia	5.71	17	35.80
5	water (contaminant)	18.24	18	not counted
6	pyrazine	29.23	80	8.99
7	2,6-dimethylpyrazine	38.75	108	5.71
8	phenol (contaminant ?)	77.18	94	not counted

The pyrogram of poly(ethylene imine) has very few characteristic peaks. Ethene elutes together with carbon dioxide and with air, and it is difficult to positively identify. Ammonia gives a broad and diffuse peak. Only traces of pyrazine and dimethylpyrazine are more easily identified. These compounds probably result from the cyclization of the radical fragments formed from the thermal decomposition of the polymer.

- Aniline thermosetting resins

The amino group attached to a phenyl ring activates the *o*- and *p*- positions on the benzene ring similarly to the OH group in phenols. For this reason, a condensation reaction of aniline and formaldehyde leads to the formation of polymeric compounds. However, the amino group also can react with formaldehyde, and more complex reactions occur. For example, in the condensation of an aromatic diamine such as *m*-phenylenediamine with formaldehyde, the reaction can be written as follows:



This type of polymer is used, for example, to make resins with strong anion exchange properties[5]. Because the amino groups directly connected to the aromatic ring are weak bases, further methylation can be applied to form quaternary amines that are stronger bases. Pyrolysis of this type of polymer gives indication of both type of condensation.

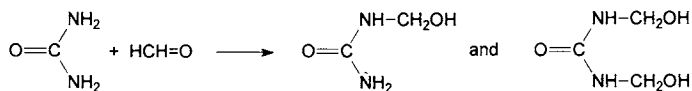
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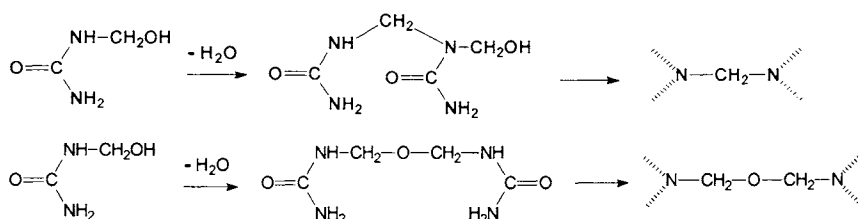
13.2 UREA THERMOSETTING RESINS

- General aspects

Urea can react with formaldehyde forming methylol compounds in reactions as shown below:



The resulting compounds may eliminate water in polycondensation reactions as follows:



The condensation reaction is typically carried out in two stages, the resulting material from the first phase of condensation being still water soluble. Urea thermosetting resins are used frequently as adhesives or as cellulose filled molding resins. After being applied in the desired form, the second condensation phase further eliminates water to form a crosslinked polymer. As seen from their structure, these polymers also contain amino nitrogens in their molecules. Melamine also can be co-condensed with urea to form a range of melamine urea formaldehyde (MUF) resins (see Section 15.3). Urea formaldehyde molding materials have many practical applications due to their good mechanical characteristics (rigidity, surface hardness, scratch resistance), solvent resistance, high flame retardance, good color retention, and good electrical insulating properties. The resistance to heating of urea formaldehyde resins is relatively good; the polymer starts decomposing at temperatures above 200°C . A study on the thermal decomposition of poly(ethyleneurea formaldehyde) resin when heated from ambient to 600°C showed the formation of volatile compounds such as NH_3 , CO_2 , HCN , CH_4 , CO and also of isocyanate, ketamine and carbodiimide or cyanogen compounds. The higher boiling fraction (77% of total volatiles) consists of chain fragments up to pentamer, including N-methylethylene urea, corresponding unsaturated compounds and higher homologs, N,N'-dimethylethylene urea and homologs [1].

References 13.2

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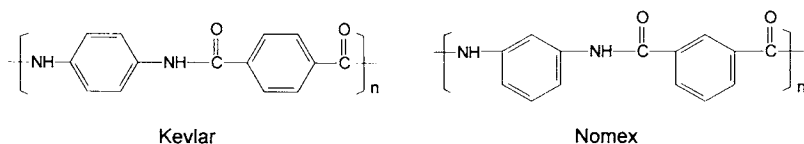
13.3 POLY(AMIDES)

- General aspects

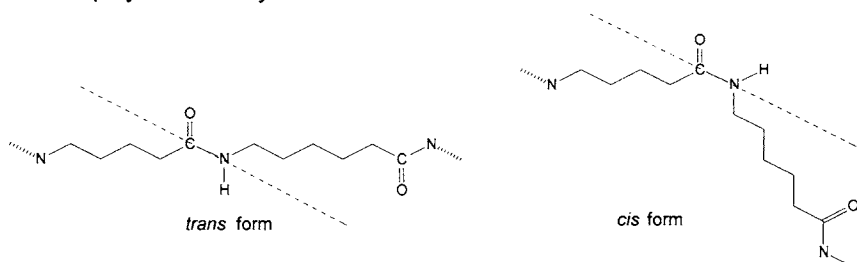
Poly(amides) include several groups of polymers with wide practical applications such as thermoplastic materials and fibers. A whole group of synthetic polyamides is known as nylons. Nylons can be generated from the polycondensation of an amino acid or from the polycondensation of a diamine and a dibasic carboxylic acid. The monomer units are connected by a peptide type bond. A specific numbering system indicates how many carbon atoms are in the monomeric unit(s). The nylons designated by a single number are amino acid polymers with the structure $[-\text{NH}-\text{R}-\text{C}(\text{O})-]_n$. For example, nylon 6 or polyamide 6 has the formula $[-\text{NH}-(\text{CH}_2)_5-\text{C}(\text{O})-]_n$. This polymer can be made from the polymerization of caprolactam in a reaction where water is added to open the caprolactam ring and then eliminated for the polycondensation step. The nylons designated by two numbers are those formed from a diamine and a dibasic acid and

have the structure $[-\text{NH}-\text{R}-\text{NH}-\text{C}(\text{O})-\text{R}'-\text{C}(\text{O})-]_n$. For example, nylon 6,6 or nylon 66 or poly(hexamethylene adipamide), also indicated as polyamide 6,6, has the structure $[-\text{NH}-(\text{CH}_2)_6-\text{NH}-\text{C}(\text{O})-(\text{CH}_2)_4-\text{C}(\text{O})-]_n$ and is one of the most common nylons. This polymer can be prepared from the hexamethylenediamine salt of adipic acid, which is dissolved in water and heated in an autoclave at $270\text{--}280^\circ\text{C}$. Besides nylon 6 and nylon 6,6, a number of other nylons are commercially available. These include nylon 3, nylon 4, nylon 7, nylon 8, nylon 11, nylon 12, nylon 4,6, nylon 6,9, nylon 6,10, nylon 10,10, nylon 6,12, nylon 6T or poly(hexamethylene-diamine-*alt*-terephthalic acid), nylon 6I or poly(hexamethylene-diamine-*alt*-isophthalic acid), etc. Some nylons have branched monomeric chains such as poly(3,3'-dimethylpropiolactam), nylon 6(3)T or poly(2,2,4-trimethylhexandiamine-*alt*-terephthalic acid), etc. Most nylons are used for fiber manufacturing. However, some are used in composite materials, in molding applications, etc.

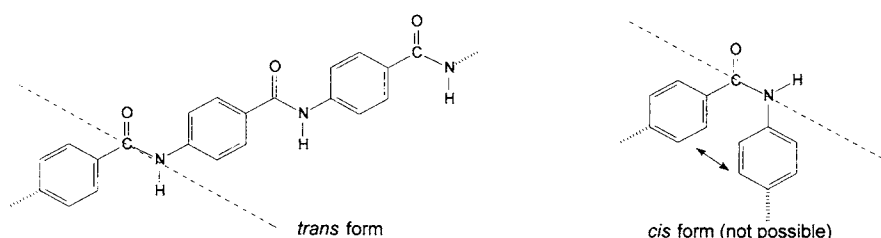
Besides the aliphatic and aliphatic/aromatic nylons, aromatic polyamides have excellent capability to form fibers. Among aromatic polyamides the most common are Kevlar® or poly(imino-1,4-phenyleneiminocarbonyl-1,4-phenylenecarbonyl) or poly(phenylene terephthalimide), and Nomex® or poly(phenylene isophthalimide). These compounds are included in a group of polyamides known as aramids. The structures of Kevlar® and Nomex® are shown below:



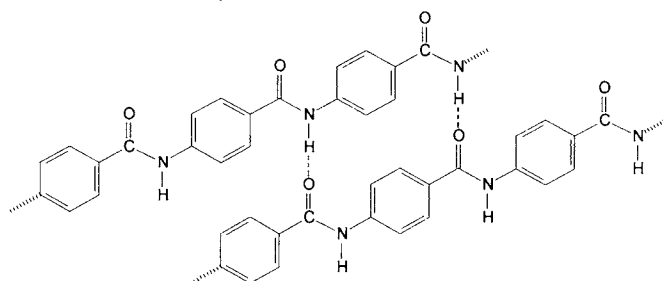
The special property to generate very strong fibers of these polymers (particularly for Kevlar®) is probably a result of their highly uniform steric structure. In a polyamide such as nylon 6, the substituents at the amide group may take a *cis* or *trans* position, which disturbs the polymer linearity as shown below:



For Kevlar® or for Nomex®, the *cis* form is not possible due to steric hindrance as indicated below:



The true spatial arrangements of the molecules are different from that shown by the planar structures, but the repulsion interactions between the two aromatic rings in *cis* form are strong enough to preclude the formation of this structure. Besides a favorable spatial arrangement, Kevlar® and to a certain extent Nomex® have hydrogen bonding between the amide groups on adjacent chains as shown below:



Hydrogen bonding adds to the strength of the fibers made from these polymers.

- Aliphatic poly(amides)

Numerous studies have been performed on thermal stability and on pyrolysis of aliphatic poly(amides) [1–12], etc.. Similarly to other classes of polymers, there is a considerable difference in the thermal stability of the polymers with aliphatic segments in their backbone and those with aromatic groups. The compounds containing aliphatic segments decompose at lower temperatures, and it is not uncommon that in addition to the cleavage of other bonds, the C–C bonds also are split. On the other hand, the aromatic rings are very resistant to thermal decomposition. The thermal decomposition of aliphatic poly(amides) was studied in connection to various practical purposes, such as the resistance of fibers to fire. Some information on thermal decomposition of aliphatic poly(amides) is summarized in Table 13.3.1 [13].

TABLE 13.3.1. Summary regarding literature information on thermal decomposition of aliphatic poly(amides) [13].

Polymer	Temp. °C	Results	Ref.
poly(iminohexamethyleneiminoadipoyl) or nylon 6,6	310–380	H ₂ O, CO ₂ , cyclopentanone, traces of saturated hydrocarbons;	14,
		purification from water and acid polymerization catalysts increases stability and decreases yield of CO ₂	15.
poly(iminohexamethyleneiminoadipoyl) or nylon 6,6	305	H ₂ O, CO ₂ , NH ₃ , cyclic monomer, cyclopentanone,	16
		cyclopentylidenecyclopentanone, cyclopentylcyclopentanone, hexylamine, hexamethyleneimine, hexamethylenediamine	

TABLE 13.3.1 (continued). Summary regarding literature information on thermal decomposition of aliphatic poly(amides) [13].

Polymer	Temp. °C	Results	Ref.
poly(iminohexamethyleneiminoadipoyl) or nylon 6,6	305	CO ₂ , NH ₃ , H ₂ O, cyclic monomer, cyclopentanone, 2-cyclopentylidenecyclopentanone, 2-cyclopentylcyclopentanone, hexylamine, hexamethyleneimine, hexamethylenediamine, 1,2,3,5,6,7-hexahydrodicyclopenta[b,e]pyridine	16
poly(iminohexamethyleneiminoadipoyl) or nylon 6,6	400	hexamethylenediamine, aminohexamethylene isocyanate, hexamethylenediamine-monocyclopentanamine, hexamethylenediaminedicyclopentanamine and larger oligomers related to above, cyclopentanone	17
poly[imino(1-oxo-dodecamethylene)] or nylon 12	800	CO ₂ , HCN, saturated and olefinic hydrocarbons C ₅ -C ₁₁ , saturated and olefinic mononitriles C _n H _(2n+1) CN and C _n H _(2n-1) CN, dodecalactam, hydrocarbons and nitrites containing amide units	18
poly[imino(1-oxo-hexamethylene)] or nylon 6	327	cyclic monomer, acetonitrile, HCN, NH ₃ , acrylonitrile, 3-cyanopropene, 4-cyanobutadiene, 4-cyano-1-butene, 5-cyano-1,3-pentadiene, 4-pentenal, 5-cyano-1-pentene, 3,5-hexadienal, 5-isocyanato-1-pentene, linear dimer	19
poly[imino(1-oxo-undecamethylene)] or nylon 11	800	CO ₂ , HCN, saturated and olefinic hydrocarbons C ₅ -C ₁₁ , saturated and olefinic mononitriles C _n H _(2n+1) CN and C _n H _(2n-1) CN, undecalactam, hydrocarbons and nitrites containing amide units	18

The curve showing the variation of weight loss % as a function of temperature (TG curve) for a 3.5 mg nylon 6 sample is shown in Figure 13.3.1. The heating was done in air between 30° C and 830° C at a rate of 10° C/min. The TGA shows that nylon 6 starts decomposing around 400° C. A small char residue is left when the TGA reaches 500° C. The char is further oxidized at higher temperatures as seen from the TGA curve.

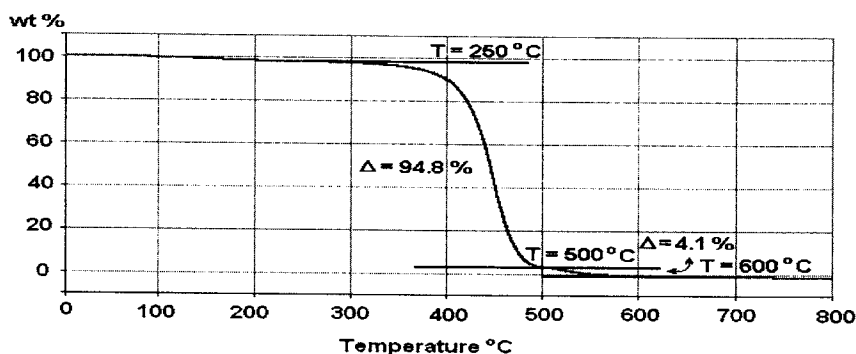


FIGURE 13.3.1. Variation of weight % loss for a nylon 6 sample in a TGA experiment at a heating rate of 10° C/min.

The results for a Py-GC/MS analysis of a polycaprolactam or nylon 6 sample, CAS# 25038-54-4, are shown in Figure 13.3.2. The pyrolysis was done at 600° C in He at a heating rate of 20° C/msec with 10 sec. THT. The separation was done on a Carbowax column (60 m, 0.32 mm i.d., 0.32 μm film thickness) with the GC starting at 40° C with a ramp of 2° C/min. up to 240° C and a final oven time of 20 min. (see Table 4.2.2). The MS was operated in EI+ mode. The peak identification for the chromatogram shown in Figure 13.3.2 was done using MS spectral library searches only and is given in Table 13.3.2.

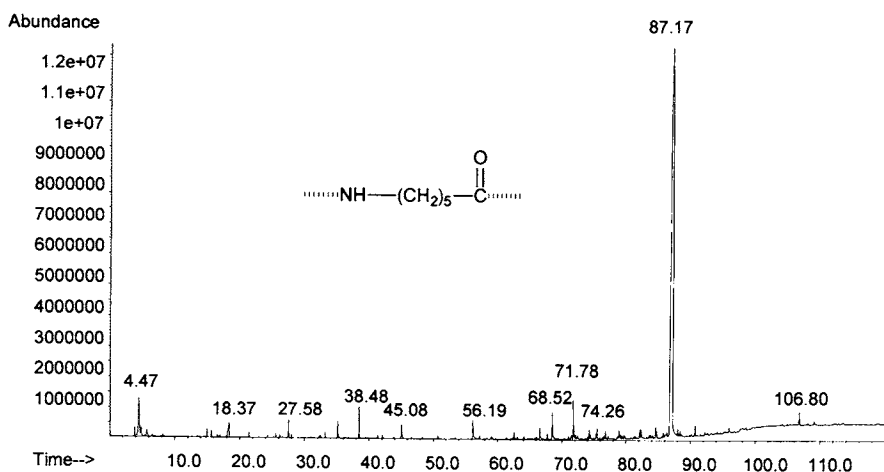
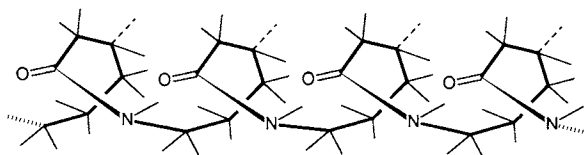


FIGURE 13.3.2. Result for a Py-GC/MS analysis of polycaprolactam or nylon 6. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

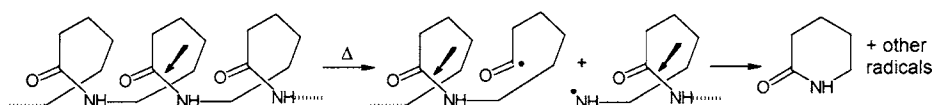
TABLE 13.3.2. Compounds identified in the pyrogram of polycaprolactam or nylon 6 shown in Figure 13.3.2.

Peak	Compound	Ret. time	MW	Area %
1	carbon dioxide	4.37	44	3.88
2	propene	4.47	42	1.00
3	butadiene	4.85	54	1.03
4	cyclopentene	5.73	68	0.95
5	1,3-cyclopentadiene	6.58	66	trace
6	2-propenenitrile	14.99	53	0.44
7	acetonitrile	15.65	41	0.39
8	water	18.35	18	1.76
9	butanenitrile	21.46	69	trace
10	cyclopentanone	27.58	84	0.96
11	pentanenitrile	27.99	83	trace
12	3-methylbut-3-enenitrile	33.19	81	trace
13	hexanenitrile	35.17	97	0.96
14	2-methyl-5-hexenenitrile?	38.48	109	1.58
15	2,4-hexadienenitrile	42.13	93	trace
16	acetic acid	45.09	63	1.10
17	butanoic acid	56.20	88	1.57
18	pentanoic acid	62.61	102	0.57
19	4-pentenoic acid	66.61	100	0.88
20	hexanoic acid	68.53	116	1.92
21	5-hexenoic acid	71.80	114	2.33
22	1-acetylazepine ?	74.27	139	0.82
23	N-acetylcaprolactam	75.53	155	0.89
24	unknown [99(100), 128(81), 58(75), 30(45), ..169(9)]	82.16		1.46
25	mix ?	82.30		1.02
26	unknown [126(100), 97(89), 69(70), 41(55), 55(55)]	84.60		0.97
27	caprolactam	87.13	113	72.56
28	unknown [179(100), 178(62), 123(39), 108(34), 95(28)]	106.80		0.97

Pyrolysis of nylon 6 generates a significant proportion of caprolactam, which can be considered the monomer. The cleavage of the peptide bond explains easily the formation of the monomer. The molecules of polymers have a spatial arrangement and do not have a linear form as typically indicated with planar chemical formulas (see also Section 1.3). The idealized spatial form for the molecule of nylon 6 is suggested below:



Under the influence of heat, the C(O)–NH bonds break, generating free radicals that continue to react, forming caprolactam as shown below:



The acetylation of the end groups of nylon 6 diminishes the thermal degradation at around 250° C, which suggests that end groups play an important role in this reaction [20, 21], assumed to have a radicalic "bite back" type mechanism.

In addition to the previous reaction other fragmentations take place, and the resulting pyrogram is quite complex [5, 22]. This complexity can be seen, for example, in Figure 13.3.3, which is the time window between ~15 min. and ~85 min. from the pyrogram already given in Figure 13.3.2.

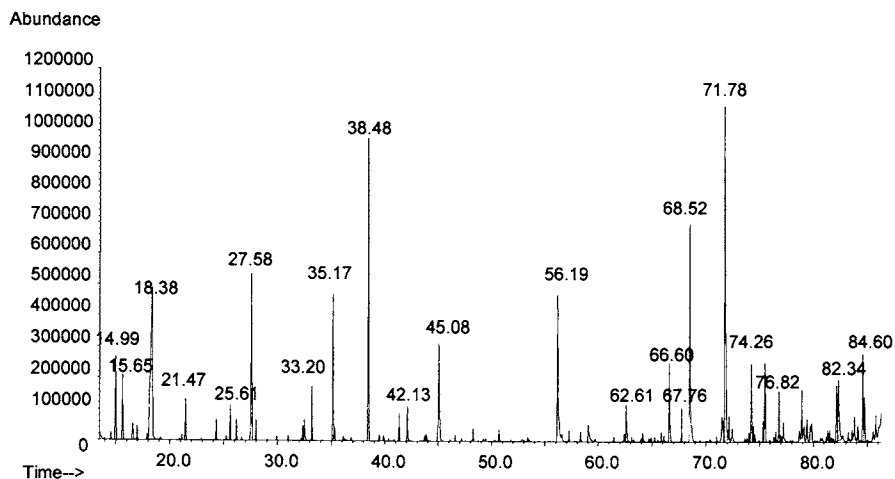
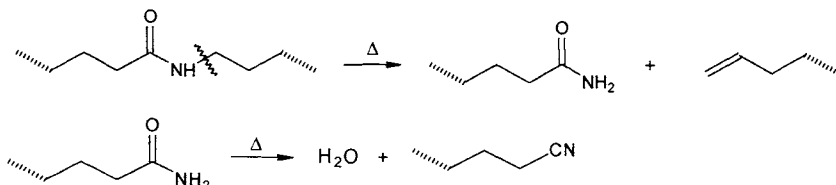
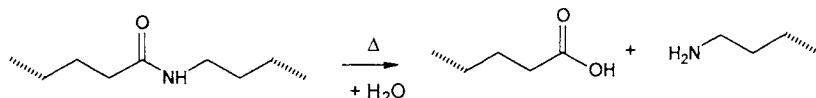


FIGURE 13.3.3. Time window between ~15 min. and ~85 min. from the pyrogram shown in Figure 13.3.2 for the pyrolysate of nylon 6.

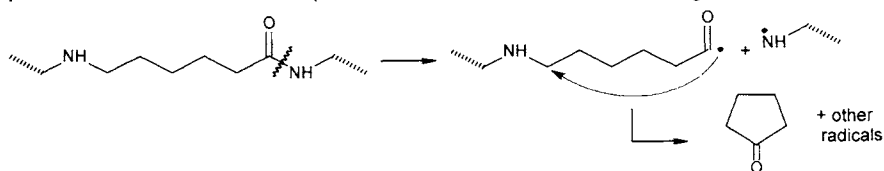
The compounds indicated in Table 13.3.2 corresponding to some of the peaks shown in Figure 13.3.3 belong to compounds resulting from the cleavage of various bonds in the polymer besides the peptide bond $C(O)-NH$, including $C-N$, $C-C(O)$ and $C-C$ bonds. The breaking of the $C-N$ bond leads to the formation of an amide and an unsaturated hydrocarbon end. Further elimination of water leads to the formation of nitriles. These types of reactions are shown below:

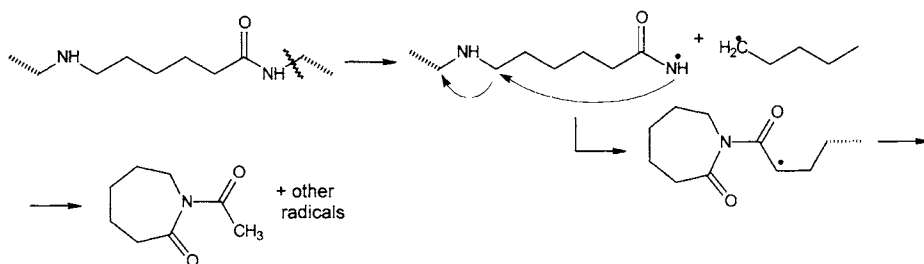


Thermal cleavage of the peptide bond in the presence of water leads to the formation of amines and acids as shown below:

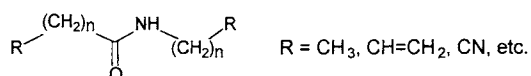


The previous reactions are shown only for the cleavage of one bond in the molecule, but the formation of small molecules involves the breaking of a second bond. Various combinations of previous reactions are possible. In addition, the cleavage of $C-C$ bonds leads to the formation of small molecules with different numbers of carbon atoms. Even hydrocarbons are formed (propene, butadiene), some of them cyclic compounds (cyclopentene, 1,3-cyclopentadiene), which indicate the radicalic mechanism of the process. Besides hexanenitrile, other nitriles are formed from $C-C$ bond cleavage in molecules with a CN end group. Among these are acetonitrile, 2-propenenitrile, butanenitrile, pentanenitrile, 2,4-hexadienenitrile, and also isomer forms such as 3-methylbut-3-enenitrile and possibly 2-methyl-5-hexenenitrile (?) resulting from free radical termination reactions. Several acids also were detected in the pyrolysate including acetic acid, butanoic acid, pentanoic acid, 4-pentenoic acid, hexanoic acid, and 5-hexenoic acid resulting from thermal hydrolysis to generate an acid chain end, followed by $C-C$ bond cleavage. Cyclization reactions also occur during pyrolysis. In addition to the formation of caprolactam, other "bite back" reactions may occur. Examples of this type of reaction with formation of cyclopentanone and N-acetyl caprolactam are shown below (the arrows show the free radical migration):

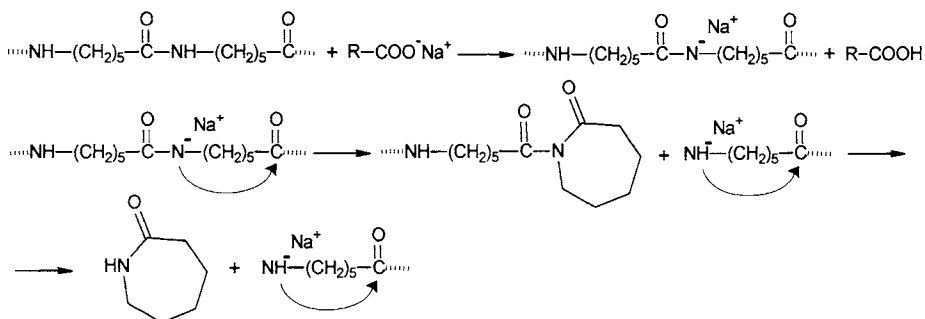




The possibility of the formation of fragments containing the amide group inside the small molecule and possibly end groups such as nitrile also is reported in literature [5, 23]. The structures of these types of molecules are shown below:



Several other pyrolytic studies were performed on nylon 6. In one such study [4], the influence of several aliphatic carboxylates on nylon 6 thermal degradation was studied. The carboxylates that were evaluated include sodium butyrate, sodium caproate, sodium α -ethylcaproate, sodium caprylate, sodium laurate, potassium caproate, potassium laurate, and lithium caproate. Small amounts of these aliphatic carboxylates strongly increase the thermal decomposition rate even at 280°C. The effect of aliphatic carboxylates can be explained by the deprotonation of one of the amide groups of the polymer followed by the nucleophilic substitution of a neighboring carbonyl group, in a reaction as shown below:



A similar behavior with that of nylon 6 can be seen during pyrolysis of nylon 12 or polylauryllactam, CAS# 24937-16-4, which has the idealized formula $[-\text{NH}(\text{CH}_2)_{11}\text{CO}]_n$. The results for a Py-GC/MS analysis of a nylon 12 sample are shown in Figure 13.3.4. The pyrolysis was done in similar conditions as for other examples, at 600°C in He, and the separation was done on a Carbowax column (see Table 4.2.2). The peak identification was done using MS spectral library searches only and is given in Table 13.3.3.

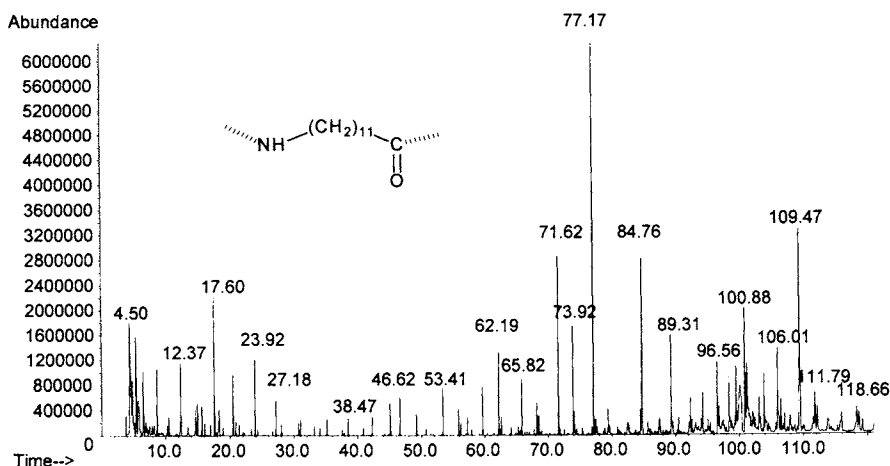


FIGURE 13.3.4. Result for a Py-GC/MS analysis of polylauryllactam or nylon 12. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 13.3.3. Compounds identified in the pyrogram of polylauryllactam or nylon 12 shown in Figure 13.3.4.

Peak	Compound	Ret. Time	MW	Area %
1	propane	4.50	44	5.85
2	2-methyl-1-propene	4.65	56	trace
3	1,3-butadiene	4.8	54	trace
4	1-pentene	4.91	70	2.01
5	hexane	5.11	86	trace
6	1-hexene	5.43	84	3.29
7	cyclopentene	5.75	68	1.11
8	heptane	5.90	100	0.74
9	1-heptene	6.55	98	2.03
10	1-methylcyclopentene	6.93	82	0.43
11	methylcyclohexane	7.11	98	trace
12	octane	7.54	114	trace
13	cyclohexene	7.95	82	trace
14	4,4-dimethylcyclopentene	8.22	96	trace
15	1-octene	8.70	112	1.76
16	1,7-octadiene	10.29	110	trace
17	nonane	10.49	128	0.53
18	1-nonene	12.37	126	1.67
19	1-methyl-2-(2-propenyl)cyclopentane (<i>trans</i>)	13.45	124	trace
20	1,8-nonadiene	14.67	124	0.67
21	2-propenenitrile	15.00	53	0.74
22	acetonitrile	15.65	41	0.76
23	hydrocyanic acid	16.57	27	trace
24	2-propenylcyclohexane ?	17.60	124	2.74
25	mix propanenitrile + butylcyclohexane	16.99	55, 140	trace
26	1-decene	18.36	140	0.91
27	1,9-decadiene	20.52	138	1.15
28	undecane	20.90	156	0.29
29	butanenitrile	21.45	69	trace

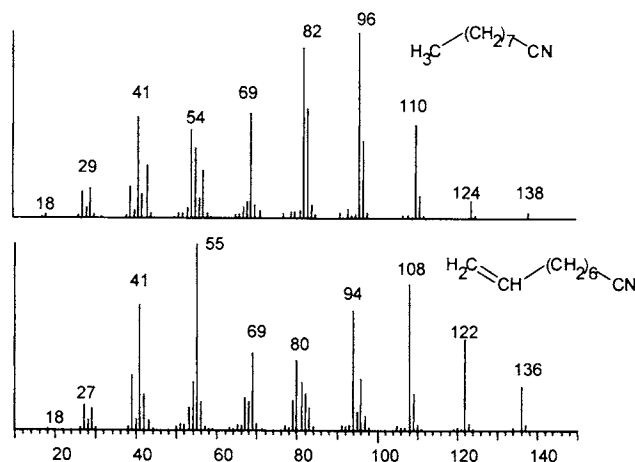
TABLE 13.3.3 (continued). Compounds identified in the pyrogram of polylauryllactam or nylon 12 shown in Figure 13.3.4.

Peak	Compound	Ret. Time	MW	Area %
30	1-undecene	23.92	154	1.36
31	1-pentylcyclopentene	24.23	138	trace
32	3-butenenitrile	26.65	67	trace
33	1,10-undecadiene	27.18	152	0.64
34	pentanenitrile	27.99	83	0.23
35	1-dodecene	30.72	168	0.23
36	heptenenitrile ?	31.01	109	0.30
37	4-cyano1-butene	33.19	81	trace
38	1,111-dodecadiene	34.04	166	trace
39	hexanenitrile	35.16	97	0.28
40	2-methyl-5-hexenenitrile	38.47	109	0.33
41	2,4-hexadienenitrile	42.13	93	trace
42	heptanenitrile	42.26	111	0.35
43	1-tetradecene	44.21	196	trace
44	acetic acid	45.10	60	0.72
45	cyclohexanecarbonitrile	46.62	109	0.72
46	octanenitrile	49.22	125	0.38
47	propanoic acid	50.69	74	trace
48	cycloheptyl cyanide	53.41	123	0.90
49	nonanenitrile	55.86	139	0.47
50	butanoic acid	56.20	88	trace
51	N-methylacetamide	57.25	73	0.32
52	8-nonenitrile	59.68	137	0.99
53	decanenitrile	62.19	153	1.62
54	pentanoic acid	62.61	102	0.36
55	N-methylbutaneamide	63.11	101	trace
56	acetamide	64.14	59	trace
57	9-decenenitrile	65.82	151	1.16
58	N-butylacetamide	67.02	115	trace
59	undecanenitrile	68.20	167	0.57
60	hexanoic acid	68.53	116	0.33
61	10-undecenitrile	71.62	165	3.55
62	N-methylhexaneamide	72.48	129	trace
63	dodecanenitrile	73.92	181	2.16
64	heptanoic acid	74.10	130	0.48
65	heptaneamide	76.31	129	trace
66	11-dodecenenitrile	77.18	179	8.75
67	N-methylheptaneamide	77.68	143	trace
68	octanoic acid	79.44	144	0.56
69	octaneamide	81.11	143	trace
70	7-octenoic acid	82.44	142	trace
71	N-methyloctanamide	82.76	157	trace
72	nonanoic acid	84.52	158	0.54
73	?-dodecenenitrile	84.76	179	4.08
74	nonaneamide	85.86	157	trace
75	N-methylnonaneamide	87.64	171	trace
76	decanoic acid	89.31	172	2.16
77	decaneamide	90.48	171	trace
78	N-methyldecanamide	92.33	185	1.01
79	N-ethyldecanamide	92.60	199	0.33
80	undecanoic acid	93.98	186	0.36
81	decanal-O-methylloxime	94.26	185	0.84
82	undecaneamide	95.06	185	0.24
83	mix	96.56		1.95

TABLE 13.3.3 (continued). *Compounds identified in the pyrogram of polylauryllactam or nylon 12 shown in Figure 13.3.4.*

Peak	Compound	Ret. Time	MW	Area %
84	N-methylundecanamide	96.86	199	0.84
85	dodecanoic acid	98.38	200	1.52
86	N-ethyldodecanamide	99.31	227	0.37
87	dodecanamide	99.47	199	1.60
88	azacycloundecan-2-one	99.66	169	0.38
89	unknown [82(100), 55(97), 110(81), 84(66), 127(54), 167(49)]	100.11		4.76
90	11-dodecenoic acid	100.88	198	3.23
91	N-methyldodecanamide	101.25	213	2.75
92	unknown oxime ?	103.14		1.03
93	N-ethylundecanamide ?	103.92	213	1.34
94	unknown oxime ?	106.01		2.92
95	unknown amide	106.49		0.89
96	azacyclotridecan-2-one	109.47	197	7.18
97	N-ethyldodeceneamide ?	111.53	225	0.75
98	N-butyldeceneamide ?	111.79	253	1.49
99	unknown	118.34		1.37
100	N-pentyldeceneamide ?	118.66	267	0.84
101	1,10-dicyanodecane	119.20	192	0.84

Similar to other examples previously discussed, some peak identifications indicated in Table 13.3.3 are only tentative. Even the spectra of some simple compounds such as 8-nonenitrile, 9-decenitrile, 10-undecenitrile, and 11-dodecenitrile are not available in common mass spectral libraries. The assignment for these unsaturated nitriles was done based on the similarity between their spectra and that of nitriles with saturated chain having the same number of carbon atoms. The spectra for the nonanenitrile and 8-nonenitrile are shown in Figure 13.3.5a, and those for dodecanenitrile and 11-dodecenitrile are shown in Figure 13.3.5b.

FIGURE 13.3.5a. *Mass spectra of nonanenitrile (MW = 139) (from NIST'98 library) and of 8-nonenitrile (MW = 137) (tentative).*

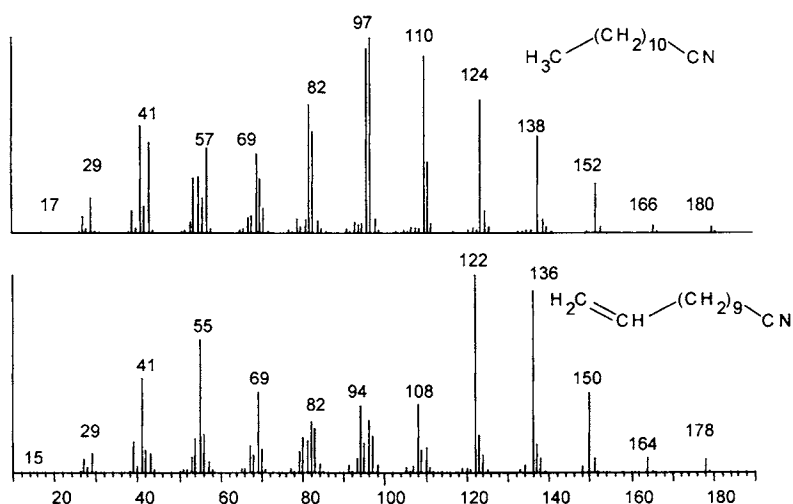
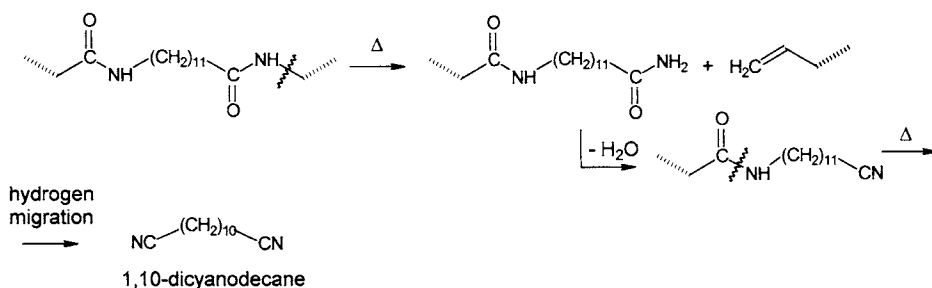


FIGURE 13.3.5b. Mass spectra of dodecanenitrile (MW = 181) (from NIST'98 library), and 11-dodecenenitrile (MW = 179) (tentative).

In spite of some difficulty in identifying some of the peaks generated during pyrolysis of nylon 12, several groups of molecules are obviously present in the pyrolysate. Among these are hydrocarbons, acids, nitriles, amides, N-substituted amides (compounds containing the amido group inside the fragment molecule such as N-methyldecanamide, N-ethyldecanamide, etc.), dinitriles (e.g. 1,10-dicyanodecane), and tentatively identified even oximes. The diversity of these molecules indicates that all bond types may be cleaved during nylon 12 pyrolysis. This includes C-C, C-N and C-O bonds. The free radical nature of the pyrolysis process is obvious in the formation of the variety of compounds shown in Table 13.3.3. The formation of 1,10-dicyanodecane is indicated below:



The number of fragment molecules obtained during pyrolysis of nylon 12 is higher than that for nylon 6. However, the similarity in the reaction types occurring during pyrolysis of the two polymers is obvious. Even formation of azacyclotridecan-2-one, which is the equivalent of caprolactam for nylon 6, takes place in the pyrolytic process of nylon 12.

To a considerable extent, pyrolysis of nylons made from a diamine and a dibasic carboxylic acid generate the same type of compounds as poly(amino acids). It includes

hydrocarbons, nitriles, amides, acids, etc. The results for a Py-GC/MS analysis of a nylon 6,6 or poly(hexamethylene adipamide) sample, CAS# 32131-17-2, are shown in Figure 13.3.6. The pyrolysis was done in similar conditions as for other examples, at 600° C in He, and the separation was done on a Carbowax column (see Table 4.2.2). The peak identification was done using MS spectral library searches only and is given in Table 13.3.4.

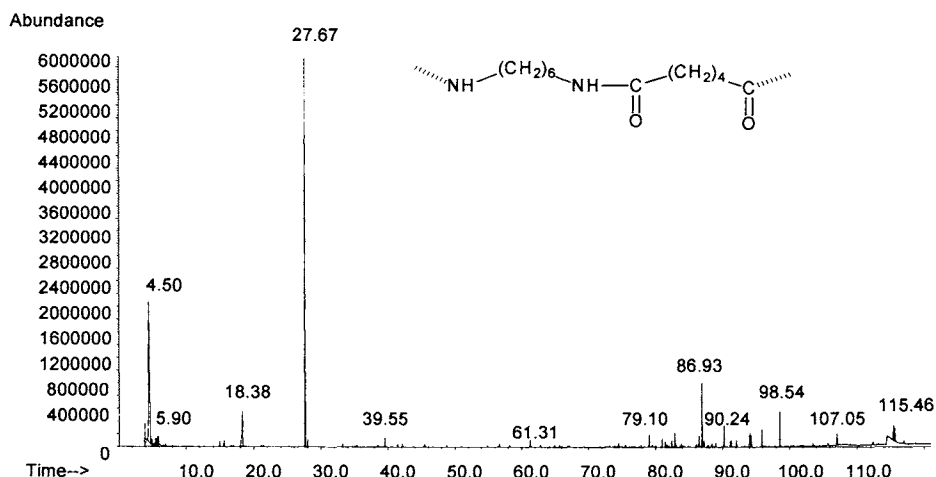


FIGURE 13.3.6. Result for a Py-GC/MS analysis of nylon 6,6 or poly(hexamethylene adipamide). Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

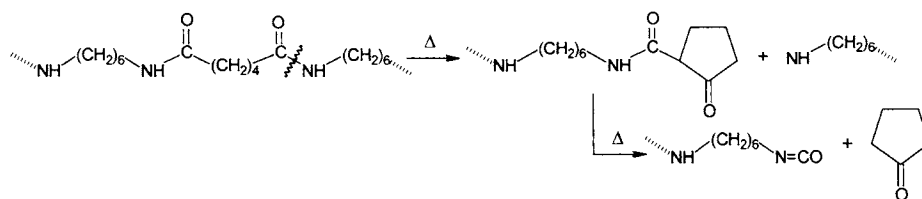
TABLE 13.3.4. Compounds identified in the pyrogram of poly(hexamethylene adipamide or nylon 6,6 shown in Figure 13.3.6.

Peak	Compound	Ret. time	MW	Area %
1	carbon dioxide	4.50	44	26.15
2	1,3-butadiene	4.90	54	trace
3	1-pentene	5.00	70	trace
4	1,3-pentadiene	5.13	68	trace
5	1-hexene	5.49	84	0.96
6	cyclopentene	5.79	68	1.55
7	1,5-hexadiene	5.90	82	0.89
8	2-propenenitrile	14.99	53	trace
9	acetonitrile	15.64	41	trace
10	hydrocyanic acid	16.57	27	trace
11	N-vinylaziridine	16.70	69	trace
12	propanenitrile	17.00	55	trace
13	water	18.38	18	5.67
14	2-butenenitrile	21.10	67	trace
15	butanenitrile	21.47	69	trace
16	2-methyl-2-propenenitrile	25.25	67	trace
17	cyclopentanone	27.67	84	38.58
18	pentanenitrile	28.05	83	0.52
19	4-cyano-1-butene	33.22	81	trace
20	2-cyclopentene-1-one	39.56	82	0.80

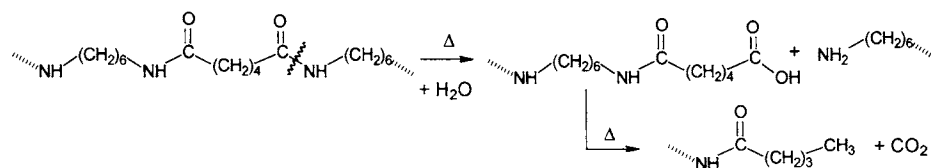
TABLE 13.3.4 (continued). Compounds identified in the pyrogram of poly(hexamethylene adipamide or nylon 6,6 shown in Figure 13.3.6.

Peak	Compound	Ret. time	MW	Area %
21	acetic acid	45.43	60	trace
22	propanoic acid	51.18	74	trace
23	2,3-1H-indole	56.71	119	trace
24	unknown (mixture ?)	61.31		0.63
25	4-methylcyclohexanone	79.10	112	1.12
26	azacyclotridecan-2-one ?	81.03	197	0.64
27	2-cyanocyclopentanone	82.45	109	0.69
28	1-methyl-3-formyl indole	82.90	159	1.28
29	unknown [111(100), 55(66), 100(42), 112(40), 154(39), ... 183(18)]	86.51		1.08
30	caprolactam	86.93	113	5.84
31	2,6-dimethyl-1,4-dihydropyridine-3,5-dicarbonitrile	87.20	159	trace
32	hexanedinitrile	90.24	108	1.91
33	2-methyl-6-ethyl-1,4-dihydropyridine-3,5-dicarbonitrile	92.09	173	0.56
34	unknown [128(100), 111(75), 69(53), 55(46), 153(20)]	94.07		1.69
35	2-oxocyclopentanecarboxamide	94.26	127	1.08
36	unknown [128(100), 111(99), 55(60), 182(52), 100(51)]	95.91		1.44
37	unknown [111(100), 128(98), 55(79), 100(35)...180(19)]	98.54		2.93
38	unknown [179(100), 178(45), 136(34), 123(34), 103(25)]	107.05		1.49
39	unknown [176(100), 92(46), 89(44), 148(35), 91(31)]	115.46		2.50

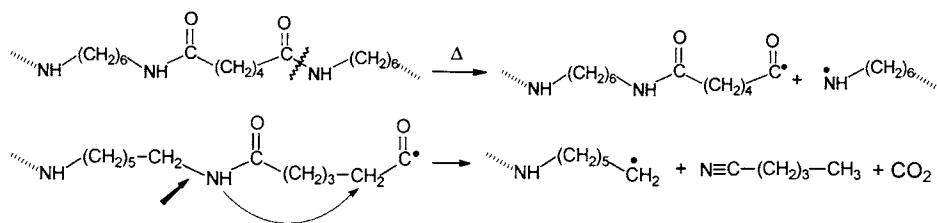
The main volatile compounds formed in this reaction are cyclopentanone. The mechanism of this reaction involves a hydrogen transfer reaction [17]:



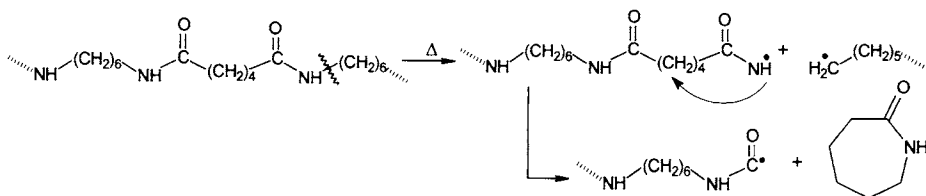
Carbon dioxide also is generated during the pyrolysis of diamine/dibasic carboxylic acid polymers, and its level is significantly higher compared to that produced in the pyrolysis of poly(amino acids). Several mechanisms can explain the formation of CO_2 . One of the possibilities involves the formation of water during pyrolysis, which leads to an acid that is decarboxylated as shown in the following reactions:



Another possible path for the formation of CO_2 is shown below:



Among other pyrolysate components nylon 6,6 also generates some caprolactam (about 6%). The formation of this compound can be explained schematically by the following reactions (the arrow shows the free radical "bite back" reaction) [24]:



One more example of flash pyrolysis is given below for nylon 6,10 or poly(hexamethylene sebacamide), CAS# 9008-66-6, with the idealized formula $[-\text{NH}(\text{CH}_2)_6\text{NHCO}(\text{CH}_2)_8\text{CO}]_n$. The Py-GC/MS results are shown in Figure 13.3.7. The pyrolysis was done in similar conditions as for other examples, at 600° C in He, and the separation was done on a Carbowax column (see Table 4.2.2). The peak identification was done using MS spectral library searches only and is given in Table 13.3.5.

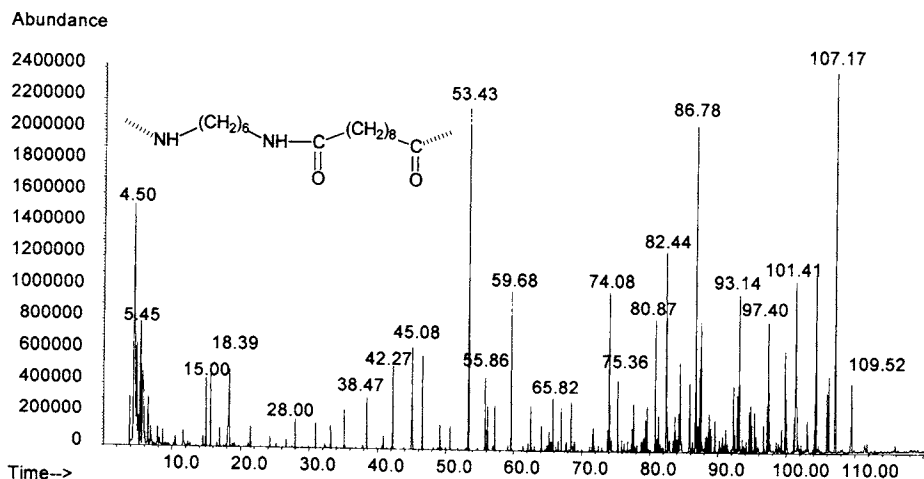


FIGURE 13.3.7. Result for a Py-GC/MS analysis for nylon 6,10 or poly(hexamethylene sebacamide). Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 13.3.5. Compounds identified in the pyrogram for poly(hexamethylene sebacamide) or nylon 6,10 shown in Figure 13.3.7.

Peak	Compound	Ret. Time	MW	Area %
1	ethene	4.40	28	trace
2	1-propene	4.46	42	trace
3	carbon dioxide	4.50	44	5.98
4	2-methylpropene	4.54	56	4.88
5	butadiene	4.80	54	3.20
6	ethylcyclopropane	4.90	70	trace
7	2-butene ?	4.59	56	trace
8	1,4-pentadiene	5.10	68	0.86
9	1-hexene	5.49	84	3.39
10	cyclopentene	5.77	68	3.21
11	1,5-hexadiene	5.89	82	trace
12	4-methylcyclopentene	6.09	82	trace
13	2,4-hexadiene(E,Z)	6.32	82	trace
14	1-heptene	6.55	98	1.40
15	1,3-hexadiene	6.94	82	0.40
16	cyclohexene	7.95	82	0.45
17	2-propenenitrile	15.00	53	1.28
18	acetonitrile	15.65	41	1.44
19	hydrocyanic acid	16.57	27	trace
20	N-vinylaziridine	16.70	69	trace
21	propanenitrile	17.00	55	0.32
22	water	18.39	18	2.82
23	2-butenenitrile	21.10	67	trace
24	butanenitrile	21.47	69	0.32
25	3-butenenitrile	26.65	67	trace
26	pentanenitrile	28.00	83	0.42
27	heptenenitrile ?	31.01	109	0.44
28	4-cyano-1-butene	33.21	81	0.37
29	hexanenitrile	35.17	97	0.59
30	2-methyl-5-hexenenitrile	38.47	109	0.82
31	heptanenitrile	42.27	111	1.34
32	acetic acid	45.08	60	2.08
33	cyclohexanecarbonitrile	46.62	109	1.55
34	octanenitrile	49.22	125	0.38
35	propanoic acid	50.69	74	0.38
36	cycloheptyl cyanide	53.43	123	5.95
37	nonanenitrile	55.86	139	1.12
38	butanoic acid	56.18	88	0.76
39	N-methylacetamide	57.26	73	0.73
40	8-nonenenitrile	59.68	137	2.69
41	decanenitrile	62.19	153	trace
42	pentanoic acid	62.56	102	0.78
43	N-methylbutaneamide	63.11	101	trace
44	acetamide	64.14	59	0.40
45	9-decenenitrile	65.83	151	0.95
46	N-butylacetamide	67.03	115	0.62
47	hexanoic acid	68.49	116	0.79
48	N-methylpentaneamide	69.16	115	trace
49	10-undecenitrile	71.61	165	0.25
50	5-hexenic acid	71.77	114	0.51
51	N-methylhexaneamide	72.48	129	trace
52	heptanoic acid	74.08	130	2.78
53	N-pentylacetamide	74.44	129	trace

TABLE 13.3.5 (continued). *Compounds identified in the pyrogram for poly(hexamethylene sebacamide) or nylon 6,10 shown in Figure 13.3.7.*

Peak	Compound	Ret. Time	MW	Area %
54	unknown [30(100), 43(92), 72(68), 73(64), 85(62), 60(57)]	75.36		1.13
55	N-ethylhexaneamide	77.46	143	0.49
56	N-methylheptaneamide	77.69	143	0.68
57	octanoic acid	79.45	144	0.75
58	N-hexylacetamide ?	79.66	143	0.77
59	N-ethylheptaneamide	80.87	157	2.10
60	7-octenoic acid	82.44	142	3.88
61	N-heptylacetamide	82.66	157	trace
62	nonanoic acid	84.50	158	1.84
63	8-nonenoic acid	85.89	156	1.46
64	mix	88.64		0.33
65	unknown [142(100), 85(80), 57(71), 141(51), 41(44), 102(44)]	88.76		0.63
66	N-octylacetamide	89.60	171	0.52
67	N-nonylacetamide	92.29	185	1.25
68	N-ethyl-?-deceneamide	93.14	197	2.69
69	N-propyldecaneamide ?	94.62	213	0.63
70	unknown amide	94.81		0.81
71	nonylamide ?	94.98	171	0.39
72	unknown	97.40		2.55
73	unknown	99.83		1.74
74	unknown	104.21		1.01
75	mix	104.36		3.49
76	12-aminolauric acid	105.97	215	1.31
77	unknown [198(100), 99(62), 98(56), 55(53), 141(51), 158(34)]	106.23		1.70
78	decanedinitrile	107.17	164	9.50
79	azacyclotridecan-2-one	109.52	197	1.88

The pyrogram of nylon 6,10 contains a considerable number of peaks. This can be explained easily by the numerous possibilities of bond cleavages for this polymer. However, regarding pyrolysis mechanisms and functionalities generated for this polymer, there are no significant differences compared to the pyrolysis of nylon 6,6.

In addition to Py-GC/MS in the analysis of polyamides, Py/MS has been used for the same purpose [3, 25]. A dependence between the mass of an ion and the corresponding structure of the fragment can be established for a number of compounds characteristic for each polymer, allowing identifications.

- Aromatic poly(amides)

Aromatic polyamides (aramids) are typically prepared from the reaction below 95° C of the aromatic diacid chlorides with the diamine in a solvent such as *N*-methyl pyrrolidone containing some calcium chloride, which helps to keep the growing polymer in solution. The polymer can be further dried and dissolved in sulfuric acid to form a solution utilized for the spinning of fibers. The resulting fibers have excellent mechanical properties as well as better thermal stability compared to the aliphatic nylons. From the two most common aramids Kevlar® has the best mechanical properties and very high impact resistance, while Nomex® has a higher thermal stability. Aramid fibers can survive temperatures up to 500° C and do not melt, retaining good mechanical properties even when heated in air for as long as two weeks at temperatures around 300° C. They have

many practical applications for making industrial fibers used in tire industry, manufacturing of fire protective equipment, and applications in making composite materials. Some pyrolysis studies on aromatic polyamides are reported in literature [26–29]. Information on thermal decomposition of aramids in general is also available, part of it being summarized in Table 13.3.6 [13].

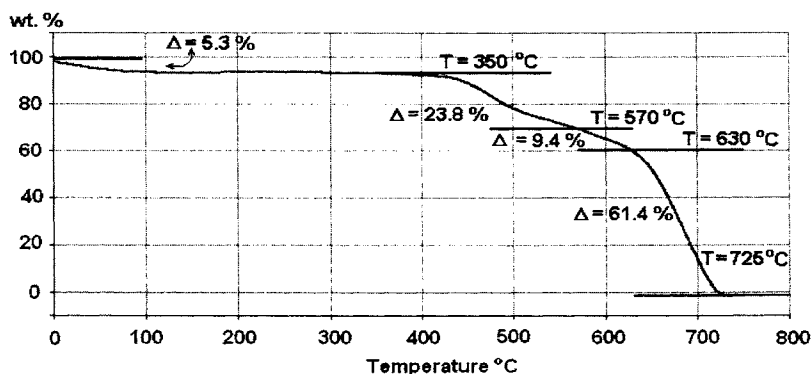
TABLE 13.3.6. Summary regarding literature information on thermal decomposition of aramids [13].

Polymer	Temp. °C	Results	Ref.
poly(1,4-piperazinediyl-terephthaloyl)	475	after 1 h, 21.1% residue, 45.6% chain fragments, 33.3% volatiles comprising mainly H ₂ O, CO, H ₂ , CO ₂ , NH ₃ , with traces of hydrocarbons, pyrazines, and pyrroles	30
poly(2,5-dimethyl-1,4-piperazinediyl-isophthaloyl)	475	after 1 h, 5.1 % residue, 73.8% chain fragments, 20.5% volatiles comprising mainly CO, H ₂ O, CH ₄ , CO ₂ , H ₂ , with traces of hydrocarbons, pyrazines, pyrroles	30
poly(2,5-dimethyl-1,4-piperazinediyl-oxaloyl)	475	after 1 h, 1% residue, 73.5% chain fragments, comprising mainly CO, with traces of H ₂ , CO ₂ , H ₂ O, hydrocarbons, pyrazines, pyrroles	31
poly(2,5-dimethyl-1,4-piperazinediyl-terephthaloyl)	475	after 1 h, 9.4% residue, 3.2% chain fragments 87.4% volatiles comprising mainly CO, H ₂ O, CO ₂ , CH ₄ , NH ₃ , with traces of hydrocarbons, pyrazines, and pyrroles	31
poly(2-methylpiperazinediyl-terephthaloyl)	475	after 1 h, 11.3% residue, 46.2% chain fragments, 42.5% volatiles comprising mainly CO, H ₂ O, CO ₂ , CH ₄ , NH ₃ , H ₂ , with traces of hydrocarbons, pyrazines, and pyrroles	30
poly(iminoisophthaloyl-co-terephthaloyl-imino-1,4-phenylene)	250–620	36% residue, 24% chain fragments, 40% volatiles comprising H ₂ , CO, CO ₂ , CH ₄	32
poly(iminoisophthaloyl-imino-1,3-perchlorophenylene)	550	H ₂ O (46 mol%), CO (18), CO ₂ (31), CH ₄ (1.2), HCN (1.3), and smaller quantities of, N ₂ O, NO, CH ₃ Cl, ethylene, acetylene, cyanogen, acetonitrile, acetone, acetic acid, cyanogen chloride, propenenitrile, benzene, toluene, benzonitrile, phenol, chlorobenzene	26
poly(iminoisophthaloyl-imino-1,3-phenylene) (Nomex)	300–500	mixture of H ₂ , CO, CO ₂ , H ₂ O, HCN, benzene, toluene, benzonitrile	33
poly(iminoisophthaloyl-imino-1,3-phenylene) (Nomex)	ambient to 800	breaking of hydrogen bonds takes place between 300–400° C; above 433° C formation of certain heterocycles occurs associated by the breaking of amides and formation of amines and carbonyl groups; above 607° C total disappearance of amide groups is noticed; as temperature increases further condensations occur with char formation	34
poly(iminoisophthaloyl-imino-1,3-phenylene) (Nomex)	300–500	CO ₂ , H ₂ O, CO	35
poly(iminoisophthaloyl-imino-1,3-phenylene) (Nomex)	450–550	benzene, HCN, toluene, benzonitrile, H ₂ , CO, CO ₂ , H ₂ O, benzene, benzonitrile, 1,3-dicyanobenzene, 3-cyanobenzoic acid, other trace compounds	35, 26
poly(iminoisophthaloyl-imino-1,4-phenylene)	300–500	mixture of H ₂ , CO, CO ₂ , H ₂ O, HCN, benzene, toluene, benzonitrile	33
poly(iminoterephthaloyl-imino-1,3-phenylene)	300–500	mixture of H ₂ , CO, CO ₂ , H ₂ O, HCN, benzene, toluene, benzonitrile	33
poly(iminoterephthaloyl-imino-1,4-phenylene) or Kevlar	300–500	mixture of H ₂ , CO, CO ₂ , H ₂ O, HCN, benzene, toluene, benzonitrile	33
poly(iminoterephthaloyl-imino-1,4-phenylene) or Kevlar	370–450	CO ₂ , H ₂ O, CO	35

TABLE 13.3.6 (continued). *Summary regarding literature information on thermal decomposition of aramids [13].*

Polymer	Temp. °C	Results	Ref.
poly(iminoterephthaloyl-imino-1,4-phenylene) or Kevlar	450–550	benzene, HCN, toluene, benzonitrile, H ₂	35
poly(iminoterephthaloyl-imino-1,4-phenylene) or Kevlar	527	cyanobenzene, dicyanobenzene, aniline, 1,4-diaminobenzene, 4-cyanoaniline, benzaldehyde, benzene, CO, NH ₃ , CO ₂ , H ₂ O, benzamide, benzoic acid, phenylisocyanate, terephthaldehyde, benzanilide, NH ₂ -Ph-NH-CO-Ph, NC-Ph-NH-CO-Ph, NH ₂ -Ph-NH-CO-Ph-CN, Ph-NH-CO-Ph-CHO	19

The curve showing the variation of weight loss % as a function of temperature (TG curve) for a 3.5 mg poly(phenylene isophthalamide) or Nomex[®] fiber sample is shown in Figure 13.3.8. The heating was done in air between 30° C and 830° C at a rate of 10° C/min. The TGA shows an initial loss of weight below 100° C. This is due to the evaporation of water adsorbed on the Nomex[®] fibers used as a sample. The polymer shows some decomposition starting at 400° C, but the process is slow and takes place in several stages when the heating is continued. It ends with the formation of a char type material with unknown composition. The last step in the TGA curve is caused by the oxidation of the char residue (carbon accounts for about 70% of the polymer).

FIGURE 13.3.8. *Variation of weight % loss for a Nomex[®] sample in a TGA experiment at a heating rate of 10° C/min.*

The Py-GC/MS results for a poly(phenylene isophthalamide) or Nomex[®] sample are shown in Figure 13.3.9. The pyrolysis was done at 850° C in He, with the rest of the conditions similar to those used for other examples previously discussed (see Table 4.2.2). Higher temperature was necessary for the sample since Nomex[®] decomposes more slowly at temperatures used, for example, for the pyrolysis of aliphatic nylons. The separation of the pyrolysate was done on a Carbowax column in the same conditions used for other polymers. The peak identification was done using MS spectral library searches only and is given in Table 13.3.7.

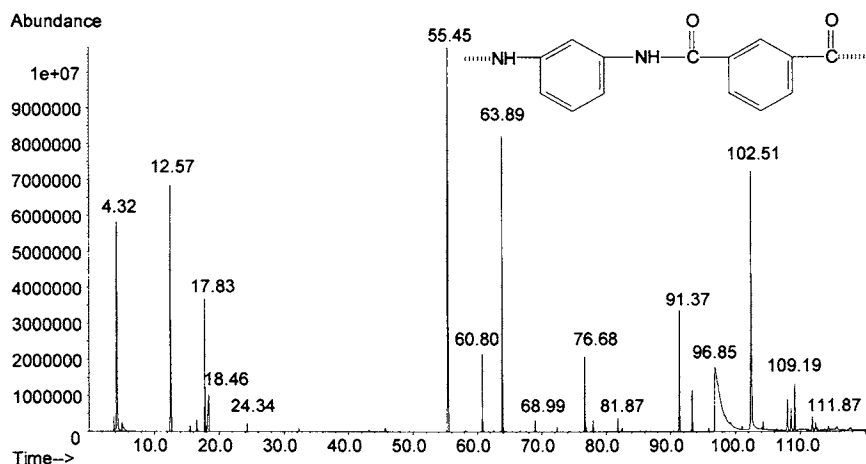


FIGURE 13.3.9. Result for a Py-GC/MS analysis for poly(phenylene isophthalamide) or Nomex[®]. Pyrolysis done on 0.4 mg material at 850° C in He, with the separation on a Carbowax type column.

TABLE 13.3.7. Compounds identified in the pyrogram for poly(phenylene isophthalamide) or Nomex[®] shown in Figure 13.3.9.

Peak	Compound	Ret. Time	MW	Area %
1	carbon dioxide	4.32	44	8.99
2	methane	4.45	16	trace
3	1-pentene ?	4.69	70	trace
4	ammonia	5.09	17	0.33
5	1-hexene	5.22	84	trace
6	acetaldehyde	5.76	44	trace
7	1-heptene	6.38	98	trace
8	1,3-cyclopentadiene	6.51	66	trace
9	benzene	12.57	78	9.84
10	acetonitrile	15.56	41	0.22
11	hydrocyanic acid	16.57	27	0.42
12	propanenitrile	16.90	55	trace
13	toluene	17.83	92	3.98
14	water	18.46	18	2.58
15	1,3-dimethylbenzene	24.34	106	0.22
16	styrene	32.28	104	trace
17	N,N-dimethylacetamide	43.16	87	trace
18	acetic acid	45.63	60	trace
19	benzonitrile	55.45	103	16.62
20	4-methylbenzonitrile	58.19	117	trace
21	3-methylbenzonitrile	60.80	117	2.41
22	2-methylbenzonitrile	62.51	117	trace
23	aniline	63.89	93	10.61
24	3-methylbenzenamine (<i>m</i> -toluidine)	68.99	107	0.36
25	1,2-benzendiamine	72.41	108	0.14
26	1,1'-biphenyl	76.68	154	2.33
27	phenol	76.90	94	0.15
28	diphenylmethane	77.98	168	0.33

TABLE 13.3.7 (continued). *Compounds identified in the pyrogram for poly(phenylene isophthalamide) or Nomex® shown in Figure 13.3.9.*

Peak	Compound	Ret. Time	MW	Area %
29	3-methyl-1,1'-biphenyl	81.87	168	0.41
30	1-methyl-4-(phenylmethyl)benzene	82.41	182	trace
31	4-methyl-1,1'-biphenyl	82.51	168	trace
32	1,3-benzenedicarbonitrile	91.37	128	4.06
33	9H-fluorene	93.35	166	1.34
34	benzoic acid	96.85	122	16.46
35	2-amino-1,1'-biphenyl	101.06	169	0.13
36	1,3-benzenediamine	102.51	108	12.45
37	benzo[h]quinoline	104.32	179	0.27
38	benzamide	108.06	121	1.41
39	3-aminobenzonitrile	108.63	118	0.99
40	p-phenylbenzonitrile	109.19	179	2.03
41	benzo[f]quinoline	111.87	179	0.62
42	2-methylacridine	112.35	193	0.33

The mechanism of thermal decomposition for poly(phenylene isophthalamide) involves the breaking of C–N, C(O)–NH, and C–C(O) bonds, while the aromatic rings remain in theory unaffected by heat. The presence of traces of aliphatic hydrocarbons are very likely due to some impurities in the polymer and are not generated from the aromatic structures. However, the thermal decomposition is associated with the formation of free radicals and migration of hydrogens. This explains for example the formation of 1,1'-biphenyl, resulting from radicalic interactions.

- Other poly(amides)

Studies on some other synthetic poly(amides) are reported in literature. One such group of poly(amides) is comprised of poly(amino acids). These polymers are related to polypeptides and proteins. Pyrolysis of model poly(amino acids) can be used for the understanding of pyrolysis processes of certain related natural polymers. In one such study, pyrolysis products of poly(amino acids) were examined using matrix assisted laser desorption ionization-time of flight-mass spectrometry [36]. The polymers analyzed were poly(proline), poly(phenylalanine), poly(leucine) and methionine enkephalin-Arg-Phe oligopeptide. Each polymer was individually pyrolyzed in a quartz tube in the temperature range of 245–285 °C in a nitrogen atmosphere. After pyrolysis, the residue in the pyrolysis tube was removed and analyzed by matrix assisted laser desorption ionization-time of flight-mass spectrometry (MALDI-TOF-MS). Based on a difference of 18 mass units between the major peaks from the original peptides and the pyrolysis residues, cyclic oligomers were postulated. Digestion of the pyrolysis residues with cyanogen bromide, which selectively cleaves methionine-containing peptides, was used to substantiate the presence of cyclic product in the pyrolysates.

Several other polyamides are derived from natural poly(amino acids) that are subject to a subsequent synthetic treatment. Examples are casein, groundnut protein fiber, and zein, which after a treatment with formaldehyde led to new materials with better mechanical/solubility properties. For example, casein is a mixture of several proteins that forms 3% of milk (as casein calcium salt). Casein can be fractionated into simpler proteins designated as α , β , γ , and κ [37]. The amino acid content of casein is similar to

that of wool, but its sulfur content is only 20% that of wool. The treatment with formaldehyde of this natural polymer makes it insoluble in water and with better mechanical properties (casein-formaldehyde is also known under the trade name Galalith). Both fibers and plastic materials can be made from casein-formaldehyde polymer. Zein is obtained from corn and further processed with formaldehyde. Zein-formaldehyde polymer starts decomposing around 185° C [38]. Pyrolysis products of these materials are similar to that of the original protein (see e.g. [39]).

- Copolymers of amides

A number of polyamide copolymers are known to have practical uses. The copolymers include those with different amides such as poly(caprolactam-co-lauro lactam), poly(2,2,4-trimethyl-1,6-hexandiamine-co-2,4,4-trimethyl-1,6-hexandiamine-co-1,4-benzendicarboxylic acid), poly(ϵ -caprolactam-co-hexamethylene diamine-co-terephthalic acid), poly(hexamethylenediamine-co-terephthalic acid-co-isophthalic acid), etc. The addition of longer alkyl chains in an aromatic polymeric amide may improve some mechanical properties, but thermal resilience is in general reduced. For example, poly(hexamethylenediamine-co-*m*-xylylenediamine-co-isophthalic acid-co-terephthalic acid) starts decomposing at about 310° C, significantly lower than Nomex®, for example. The same decrease in the decomposition temperature is seen for other mixed copolymers such as nylon 12 copolymers that include cycloaliphatic and aromatic segments.

Other copolymers of polyamides include poly(glycols) sequences. Examples from this group are nylon 12-*block*-poly(tetramethylene glycol) with the idealized formula $-\text{NH}-(\text{CH}_2)_{11}-\text{C}(\text{O})_x-[\text{O}-(\text{CH}_2)_4-\text{O}]_y$ and poly[(ethylene glycol)-co-1,6-hexanediamine-co-(methylpentamethylene diamine)-co-1,4-benzenedicarboxylic acid]. Pyrolysis of these copolymers generates a mixture of compounds, some typical for amides such as nitriles and some typical for polyethers.

In addition to comonomers, nylons are frequently used in blends. The pyrolysis of blends typically shows little interaction between the compounds generated from the individual blend components. However, a study on the co-pyrolysis of several polyamides in the presence of PVC showed interactions [40]. The study was done on nylon-12, nylon-6,6 and poly(1,4-phenylene terephthalamide) (Kevlar) in the presence of poly(vinyl chloride). Polyamide-PVC mixtures (typical mass ratio 1:1) were pyrolyzed at 700 and 900°C. It was found that the presence of PVC promoted the hydrolytic decomposition routes of amide groups and volatile nitrile formation from all examined polyamides due to the hydrogen chloride eliminated from PVC under pyrolysis. In the presence of PVC, an elevated yield of alkenenitriles was observed from nylon-12. For Kevlar in the presence of PVC, it was noticed the evolution of benzeneamine, benzoic acid, benzenenitrile and benzeneisocyanate. At 900°C in the presence of PVC, an enhanced evolution of HCN from nylon-12 and nylon-6,6 was noticed.

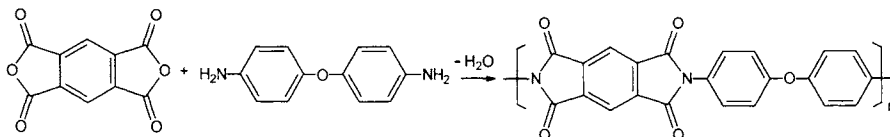
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13.4 POLY(IMIDES)

- General aspects

Poly(imides) contain the group $-C(O)-NH-C(O)-$ in their structure. Many poly(imides) with practical applications have a more complicated formula and contain oxygen atoms and aromatic rings in the backbone [1]. One example is poly(pyromellitic dianhydride-*alt*-4,4'-oxydianiline) or PMDA-ODA, CAS# 25038-81-7, which is obtained from pyromellitic anhydride and oxybis(benzenamine) by water elimination as follows:

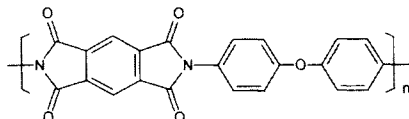


The condensation of the amino group with the pyromellitic anhydride generates in the polymer the pyromellitimide-diyl or 1,3,5,7-tetraoxo-2,3,6,7-tetrahydro-(1H,5H)-2,6-benzo[1,2c:4,5c']-dipyrrol-diyl unit. Similarly, bis-orthophthalic anhydrides connected in 5-position by a single bond or by various groups (functional spacer) such as methylene, carbonyl, oxygen, and isopropyl generate poly bis-maleimides. The formulas of a number of polymers with imide groups used in practice are given in Table 13.4.1.

TABLE 13.4.1. Names and formulas of some polyimides with practical applications.

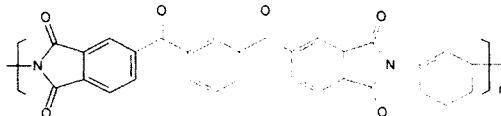
Name Poly(pyromellitic dianhydride-*alt*-4,4'-oxydianiline) or Poly(1,3,5,7-tetraoxo-2,3,6,7-tetrahydro-(1H,5H)-2,6-benzo[1,2c:4,5c']-dipyrrol-diyl-1,4-phenylene-oxy-1,4-phenylene)

Struct.



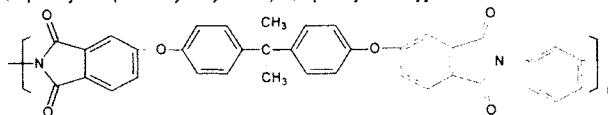
Name Poly(4,4'-isophthaloyldipthalic anhydride-*alt*-*m*-phenylenediamine). LaRC-I-TPI CAS# 115967-80-1

Struct.



Name Poly[(1,3-dihydro-1,3-dioxo-2H-isoindole-5,2-diyl)-1,3-phenylene(1,3-dihydro-1,3-dioxo-2H-isoindole-2,5-diyl)oxy-1,4-phenylene(1-methylethylidene)-1,4-phenyleneoxy]. Ultem 1000 CAS# 61128-24-3,

Struct.



Name Poly[(1,1',3,3'-tetraoxo[5,5'-bis-2H-isoindole]-2,2'-diyl)-*p,p'*-phenoxyphenyl-]

Struct.

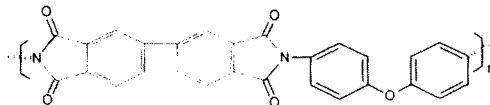
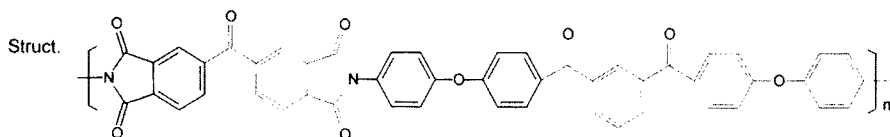
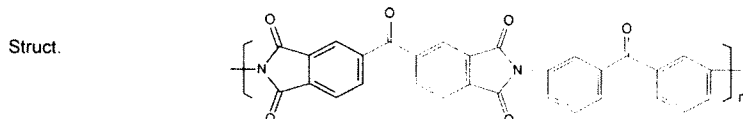


TABLE 13.4.1 (continued). *Names and formulas of some polyimides with practical applications.*

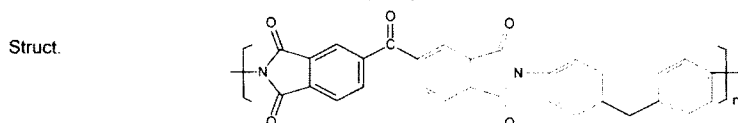
Name Poly[(1,3-dihydro-1,3-dioxo-2*H*-isoindole-2,5-diyl)carbonyl(1,3-dihydro-1,3-dioxo-2*H*-isoindole-5,2-diyl)-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,3-phenylenecarbonyl-1,4-phenyleneoxy-1,4-phenylene], LaRC-CPI CAS# 103320-42-9



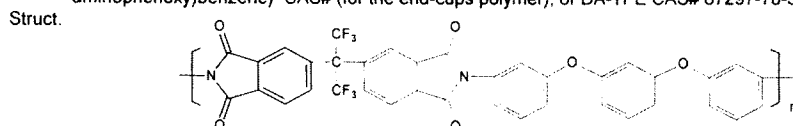
Name Poly[(1,3-dihydro-1,3-dioxo-2*H*-isoindole-2,5-diyl)carbonyl(1,3-dihydro-1,3-dioxo-2*H*-isoindole-5,2-diyl)-1,3-phenylenecarbonyl-1,3-phenylene], LaRC-TPI CAS# 51518-44-6



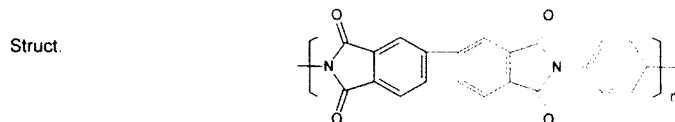
Name Poly[(1,3-dihydro-1,3-dioxo-2*H*-isoindole-2,5-diyl)carbonyl(1,3-dihydro-1,3-dioxo-2*H*-isoindole-5,2-diyl)-1,4-phenylenemethane-1,4-phenylene], PMR-15 CAS# 78392-33-3



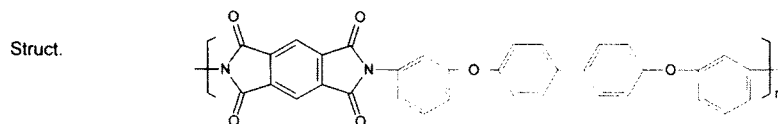
Name Poly(2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride-*alt*-1,3-bis(3-aminophenoxy)benzene) CAS# (for the end-cups polymer), 6FDA-TPE CAS# 67297-78-3



Name Poly[(1,1',3,3'-tetraoxo[5,5'-bis-2*H*-isoindole]-2,2'-diyl)-1,4-phenylene], BPDA-*p*PDCA CAS# 32197-39-0

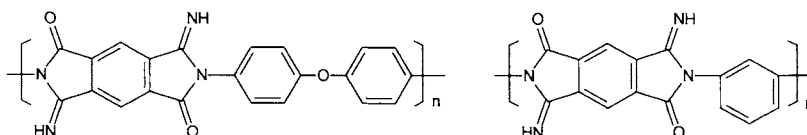


Name Poly(pyromellitic dianhydride-*alt*-3,3'-bis(4-aminophenoxy)biphenyldiamine), NEW TPI CAS# 105359-94-2



More than one nomenclature can be used for the compounds shown in Table 13.4.1. For example, when a carbonyl connects the two maleimides, the resulting unit is (1,3-dihydro-1,3-dioxo-2*H*-isoindole-2,5-diyl)carbonyl(1,3-dihydro-1,3-dioxo-2*H*-isoindole-5,2-diyl), or 5,5'-carbonylbis[1,3-isoindoldione]-2,2'-diyl.

As seen from Table 13.4.1, most of the imines contain in their structure a 3-pyrroline-2,5-dione ring (maleimide), which may suggest that this group of polymers should be included among those containing heterocycles (see Section 15.1). Being at the same time an imide, these macromolecules are discussed in this section. In addition to the pyromellitimide-diyl group, polymers with the structure shown below, also are used in practice:



The unit present in these polymers, 1,5-diimino-3,7-dioxo-2,3,6,7-tetrahydro-(1H,5H)-2,6-benzo[1,2c:4,5c']-dipyrrol-diyl, does not qualify these compounds as imides, but they also are discussed in this section.

Most of the imide type polymers have rather good thermoresistance. For example LaRC-I-TPI starts decomposing at about 510° C. Pyrolysis products of these polymers generate various fragment molecules related to the polymer structure. Several results reported in literature regarding thermal decomposition of some polymers from this class are indicated in Table 13.4.2.

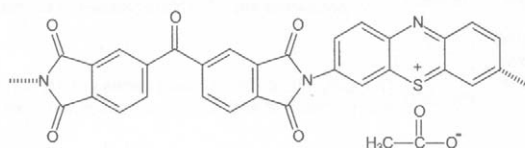
TABLE 13.4.2. Summary regarding literature information on thermal decomposition of polymers containing heterocyclic groups [2].

Polymer	Temp. °C	Results	Ref.
poly(1,5-diimino-3,7-dioxo-2,3,6,7-tetrahydro-(1H,5H)-2,6-benzo[1,2c:4,5c']-dipyrrol-diyl-1,3-phenylene)	450–500	CO, CO ₂ , HCN, NH ₃ , H ₂ and traces of CH ₄ and C ₆ H ₆ ; NH ₃ is the main product at 440° C, CO increases at higher temperatures	3
poly(1,5-diimino-3,7-dioxo-2,3,6,7-tetrahydro-(1H,5H)-2,6-benzo[1,2c:4,5c']-dipyrrol-diyl-1,4-phenyleneoxy-1,4-phenylene)	450–500	CO, CO ₂ , HCN, NH ₃ , H ₂ and traces of CH ₄ and C ₆ H ₆ ; NH ₃ is the main product at 440° C, CO increases at higher temperatures	3
poly(3,3',4,4'-benzophenone tetracarboxylic dianhydride- <i>alt</i> -2,2-bis[4-(4-amino-phenoxy)phenyl]-hexafluoropropane)	540	initial decomposition at 512°; 10% wt. loss at 540° with heat rate 10° min ⁻¹ , formation of CO, CO ₂ .	4
poly(3,3',4,4'-benzophenone-tetracarboxylic dianhydride- <i>alt</i> -diaminophenylindane)	500	decompose above 500° C	5
poly(3,3',4,4'-benzophenone-tetracarboxylic dianhydride- <i>alt</i> - <i>m</i> -phenylenediamine)	550	major products of decomposition are CO and CO ₂ ; 10% weight loss at 475 °C; 50% weight loss 790 °C, char yield 49% (in N ₂), 63% char yield at 700 °C; activation energy of decomposition 124 kJ mol ⁻¹ (N ₂); approx. 40% weight loss after heating in air at 400 °C for approx. 30 h; maximum rate of weight loss 1.74% h ⁻¹ which occurs after 14 h heating in air at 400°; maximum decomposition temp. 631°C (in N ₂)	6–8

TABLE 13.4.2 (continued). Summary regarding literature information on thermal decomposition of polymers containing heterocyclic groups [2].

Polymer	Temp. °C	Results	Ref.
poly(bis-N-phenylenemethylene-1,4-phenylene-maleimide)	350–500	benzene, toluene, aniline, succinimide, methylaniline, phenylisocyanate, tolylisocyanate, and various other products	9
poly(bis-N-phenylenemethylene-1,4-phenylene-maleimide)	350–500	aniline, phenol, succinimide, anisidine, phenylisocyanate, and various other products	9
poly(bis-N-ethylidene-maleimide) ethylidene can be replaced with $-(CH_2)_n-$, $n=6, 8, 10, 12, 1,4$ -phenylenemethylene-1,4-phenylene, or 1,4-phenylene-oxy-1,4-phenylene	350–500	aliphatic: C_2 – C_6 fractions, maleimide, succinimide, methyl maleimide, methyl succinimide, ethyl maleimide, ethyl succinimide, propyl maleimide, propyl succinimide, butyl maleimide, butyl succinimide, pentyl maleimide, pentyl succinimide, ethylidene-bis-maleimide, ethylidene-bis-succinimide, hexylidene-bis-maleimide, octylidene-bis-maleimide, decylidene-bis-maleimide, dodecylidene-bis-maleimide	9
poly(N-phenyl-maleimide)	100–400	aniline, $C_6H_5-N=CH-CH_2-CH_3$, N-phenylsuccinimide, N-phenylmaleimide (trace), $C_6H_5-N-CH-CH=CH-CO-NH-C_6H_5$	10
poly(pyromellitimide-1,4-phenylene-carbonyl-1,4-phenylene)	700	H_2 , CO, CH_4 , CO_2 , H_2O , benzene, benzonitrile, chain fragments, 60% residue	11
poly(pyromellitimide-1,4-phenylene-methylene-1,4-phenylene)	700	H_2 , CO, CH_4 , CO_2 , H_2O , benzene, toluene, benzonitrile, chain fragments, 60% residue	11
poly(pyromellitimide-1,4-phenylene-oxy-1,4-phenylene)	700	H_2 , CO, CH_4 , CO_2 , H_2O , benzene, benzonitrile, phenol, chain fragments, 60% residue	11

One polymer for which a Py-GC/MS analysis has been performed is poly(3,3',4,4'-benzophenonetetracarboxylic dianhydride-*alt*-thionin). The structure of the polymer is shown below:



This is a light sensitive polymer (λ max. 265 nm), but it has high heat resistance. For this reason, pyrolysis was performed at 850° C in He. Other conditions were kept similar to those for other examples previously described in this book (see Table 4.2.2). The separation was done on a Carbowax column. The pyrogram is shown in Figure 13.4.1. The peak identification was done using MS spectral library searches only and is given in Table 13.4.3.

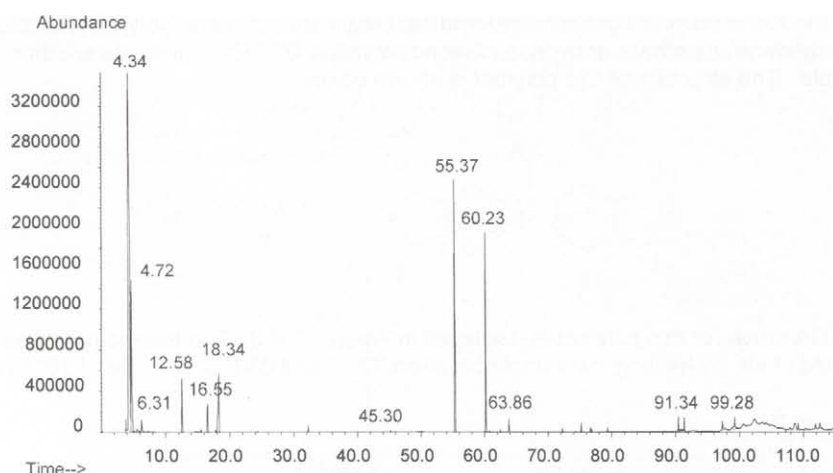
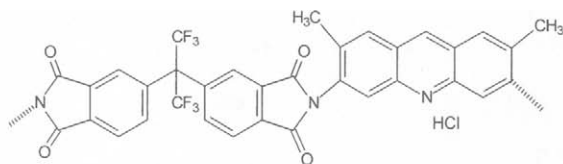


FIGURE 13.4.1. Pyrogram from Py-GC/MS analysis of poly(3,3',4,4'-benzophenone-tetracarboxylic dianhydride-alt-thionin). Pyrolysis done on 0.4 mg material at 850° C in He, with the separation on a Carbowax type column.

TABLE 13.4.3. Compounds identified in the pyrogram of poly(3,3',4,4'-benzophenone-tetracarboxylic dianhydride-alt-thionin), as shown in Figure 13.4.1.

Peak	Compound	Ret. time	MW	Area %
1	carbon dioxide	4.34	44	38.72
2	carbon oxide sulfide	4.47	60	7.71
3	hydrogen sulfide	4.72	34	12.54
4	ammonia	5.56	17	trace
5	methanethiol	5.70	48	trace
6	carbon disulfide	6.31	76	1.26
7	isocyanatomethane	7.31	57	trace
8	benzene	12.58	78	3.34
9	acetonitrile	15.54	41	trace
10	hydrocyanic acid	16.55	27	1.73
11	toluene	17.83	92	trace
12	water	18.34	18	6.48
13	butanol	24.39	74	trace
14	acetic acid	45.30	60	trace
15	benzaldehyde	50.23	106	trace
16	benzonitrile	55.37	103	13.50
17	1-methyl-2-pyrrolidinone	60.24	99	11.16
18	3-methylbenzonitrile	60.78	117	trace
19	4-methylbenzonitrile	62.49	117	trace
20	aniline	63.86	93	0.65
21	1-methyl-2,5-pyrrolidinedione	72.26	113	trace
22	benzothiazole	75.23	135	trace
23	1,1'-biphenyl	76.54	154	trace
24	phenol	76.86	94	trace
25	pyrrolidinone	79.34	85	trace
26	1,4-benzenedicarbonitrile	90.44	128	0.76
27	2-methyl-1H-isoindole-1,3(2H)-dione	90.72	161	trace
28	1,3-benzenedicarbonitrile	91.34	128	1.01
29	1,2-benzenedicarbonitrile	97.33	128	trace
30	diphenylmethanone	99.28	182	1.15

From the same class of light sensitive and heat resistant polymers, poly[4,4'-hexafluoro-isopropylidene)-diphthalic anhydride-*alt*-acridine yellow G], HCl is given as another example. The structure of this polymer is shown below:



The TGA curve for this polymer is displayed in Figure 13.4.2. The thermogram was obtained in air, by heating the sample between 30° C and 830° C at a rate of 10° C/min.

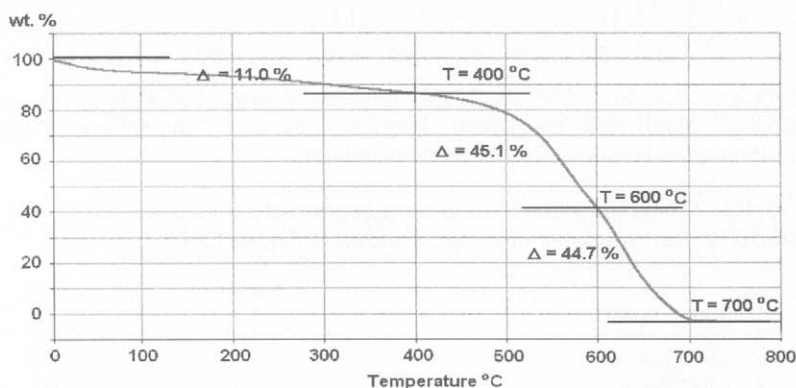


FIGURE 13.4.2. Variation of weight % loss for poly[4,4'-hexafluoro-isopropylidene)-diphthalic anhydride-*alt*-acridine yellow G] HCl in a TGA experiment at a heating rate of 10° C/min.

The TGA curve indicates a complex decomposition process. The Py-GC/MS result for poly[4,4'-hexafluoro-isopropylidene)-diphthalic anhydride-*alt*-acridine yellow G] HCl is given in Figure 13.4.3. This is a light sensitive polymer (λ max. 273 nm) but also with high heat resistance, and the pyrolysis was performed at 850° C in He. Other conditions were kept similar to those for other examples previously described (see Table 4.2.2). The separation was done on a Carbowax column. The peak identification was done using MS spectral library searches only and is given in Table 13.4.4.

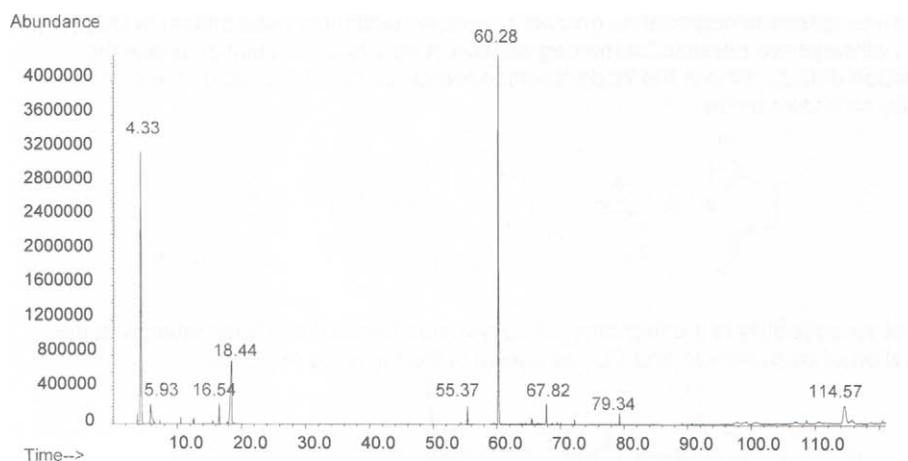


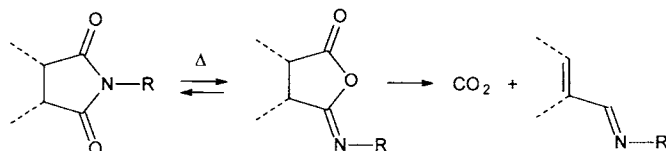
FIGURE 13.4.3. Pyrogram from Py-GC/MS analysis of poly[4,4'-hexafluoro-isopropylidene)diphthalic anhydride-alt-acridine yellow G] HCl. Pyrolysis done on 0.4 mg material at 850° C in He, with the separation on a Carbowax type column.

TABLE 13.4.4. Compounds identified in the pyrogram poly[4,4'-hexafluoro-isopropylidene)diphthalic anhydride-alt-acridine yellow G] HCl, as shown in Figure 13.4.3.

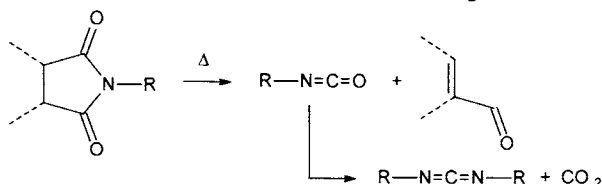
Peak	Compound	Ret. time	MW	Area%
1	carbon dioxide	4.27	44	10.55
2	trifluoromethane	4.33	70	24.00
3	acetaldehyde	5.93	44	4.35
4	isocyanatomethane	7.31	57	trace
5	methanol	10.53	32	trace
6	benzene	12.58	72	trace
7	acetonitrile	15.54	41	trace
8	hydrocyanic acid	16.54	27	2.00
9	toluene	17.83	92	trace
10	water	18.44	18	12.69
11	benzonitrile	55.37	103	1.35
12	1-methyl-2-pyrrolidinone	60.29	99	35.73
13	3,4-dimethyl-3-pyrrolin-2-one	65.48	111	trace
14	1,5-dihydro-1-methyl-2H-pyrrol-2-one	67.82	97	1.71
15	1-methyl-2,5-pyrrolidinedione	72.26	113	trace
16	pyrrolidinone	79.34	85	0.98
17	2-methyl-1H-isoindole-1,3(2H)-dione	90.72	161	trace
18	9H-carbazole	114.57	167	6.64

The decomposition products of poly(3,3',4,4'-benzophenone-tetracarboxylic dianhydride-alt-thionin) as well as that of poly[4,4'-hexafluoro-isopropylidene)diphthalic anhydride-alt-acridine yellow G] HCl generate a significant amount of CO₂. Only a few other small molecules are generated, and with relatively low structural information. Except for 2-methyl-1H-isoindole-1,3(2H)-dione, other fragments show little about the isoindoline-1,3-dione units present in the polymer. Also, fragments from thionin or from acridine yellow G either are not eluted from the chromatographic column or are too small to suggest the originating monomer.

The major gaseous degradation product of poly(N-substituted maleimides) is CO₂ [12]. Two pathways are possible for the degradation of poly(N-arylmaleimides) with the formation of CO₂. One is the imide-isoimide rearrangement followed by the elimination of CO₂ as shown below:



The other possibility is the formation of isocyanates followed by dimerization with the formation of carbodiimide and CO₂ as shown in the following reactions:

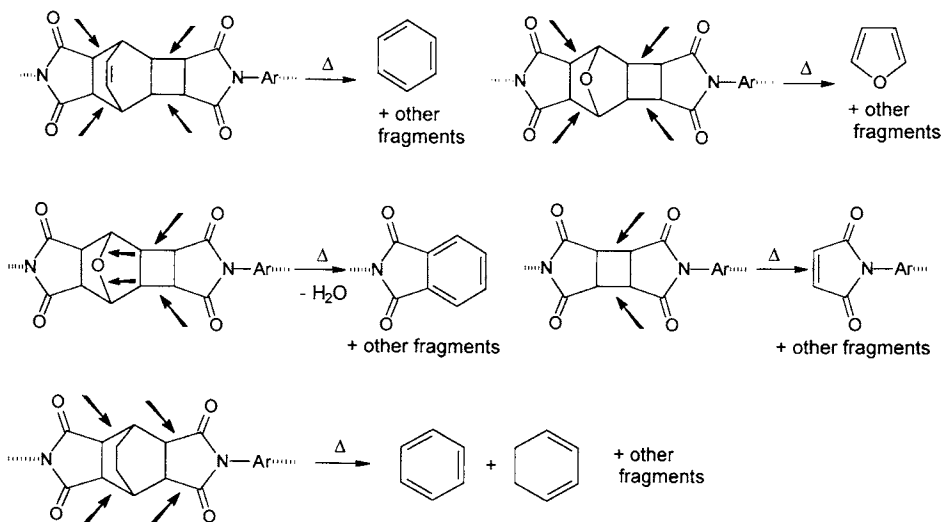


However, the formation of isocyanate and/or carbodiimide in the pyrolysate, necessary to support this mechanism, is not reported in the literature, and therefore the mechanism is not likely to occur.

A number of studies were dedicated to the understanding of the good heat resistance of the polymers from this class [13–15]. One of these studies was done to evaluate the effect of *para* substitution on the thermal degradation of poly N-arylmaleimides [16]. The effect on the degradation mechanism of poly(N-arylmaleimides) by the electron releasing and withdrawing groups from the *para* position on the N-phenyl ring was evaluated. The polymers of N-phenylmaleimide (NPMI), N-*p*-chlorophenyl-maleimide (N-*p*-CIPMI), and N-*p*-nitrophenylmaleimide (N-*p*-NO₂PMI) were obtained using benzoyl peroxide as the initiator from the synthesized monomers. Thermogravimetric study of poly(N-*p*-NO₂PMI) showed major weight loss in the temperature range 184–316° C, whereas the poly(N-*p*-CIPMI) degraded in the range 400–484° C, and the unsubstituted poly(NPMI) in 264–348° C. The energy of activation value for the degradation of poly(NPMI) (192 kJ mol) lies between those for poly(N-*p*-NO₂PMI) (138 kJ mol) and poly(N-*p*-CIPMI) (217 kJ mol). These results showed that *para* substituents have a marked effect on the imide-isoimide rearrangement, while the effect of substituents on the phenyl ring on the formation of isocyanates is minimal. Electron-releasing substituents in the *para*- and *ortho*-positions of the phenyl ring increase the electron density on the imide nitrogen. Delocalization of the electron ring density to nearby carbonyl groups would result in an increase of the strength of the -(O)C-N-C(O)- group, which will diminish the imide-isoimide rearrangement. As a result, the rearrangement and subsequent release of CO₂ may take place for the compounds with this type of substituent only at higher temperature. This is the case with poly(N-*p*-CIPMI). On the other hand, the electron-withdrawing nitro group in the *para* position of the phenyl ring reduces the electron density at the imide nitrogen. As a result the multiple bond character between the carbonyl carbon and imide nitrogen is reduced, and the imide-isoimide rearrangement is possible at lower temperature compared with the *p*-chloro

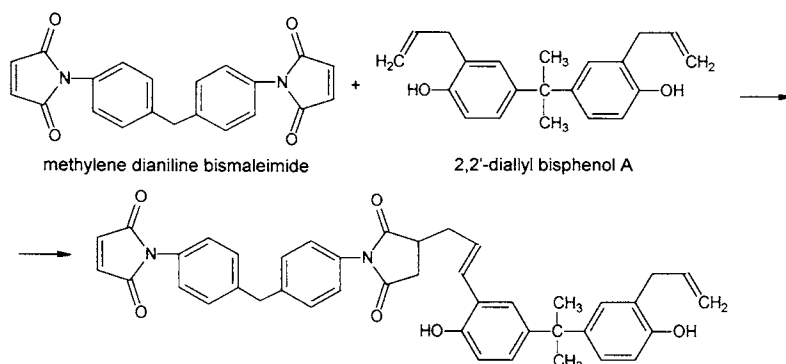
isomer. Therefore, the trend in the decomposition temperature and activation energy of degradation observed in poly(*N-p*-substituted phenyl maleimides) has been attributed to the electron donating or withdrawing nature of the substituents. Other thermal degradation products of poly(*N-p*-methylphenylmaleimide) include *N-p*-methylphenylsuccinimide, dimer and trimer of *N-p* methylphenylmaleimide, and *N,N'*-*p*-tolyliurea [17]. The major degradation product of poly(*N*-phenylmaleimide) is *N*-phenylsuccinimide [18]. The formation of trace amounts of monomer *N*-phenylmaleimide also was reported.

Another group of polymers with good heat resistance includes certain aryl-alicyclic compounds. They are generated from the polycondensation of 4,4'-diaminodiphenyl oxide with various anhydrides such as tricyclo[4,2,2,0^{2,5}]dec-9-ene-3,4,7,8-tetracarboxylic acid anhydride, 9-oxatricyclo[4,2,2,0^{2,5}]nonane-3,4,7,8-tetracarboxylic acid anhydride, cyclobutene-1,2,3,4-tetracarboxylic acid anhydride, and bicyclo[2,2,2]octane-2,3,5,6-tetracarboxylic acid anhydride. Thermal stability of these polymers is affected by the ring stability (strain) regardless the true chemical structure. Pyrolysis at 650° C generates some compounds that are the same in nature and some others that are characteristic for each polymer. The main decomposition paths, as indicated by the main pyrolysis products are shown below for each polymer (Ar = 4,4'-diphenylene oxide):

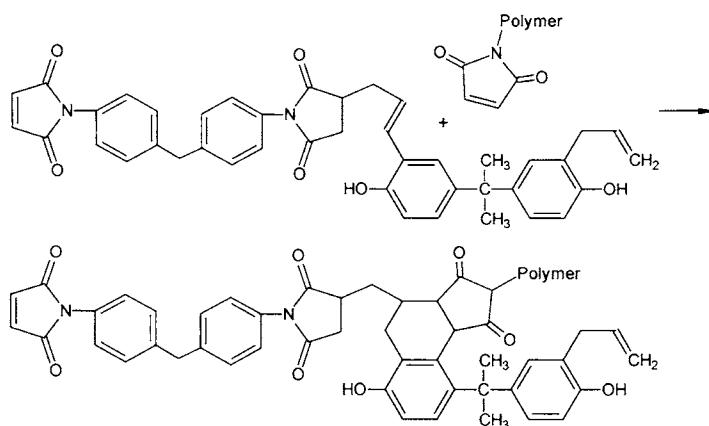


Compounds such as aniline, aminophenol, and other compounds generated from the diaminodiphenyl ether moiety are common in the pyrolysate of all polymers. The presence of specific fragments allows the polymer identification and the structure of the cycles determines the decomposition mechanism of each polymer [15].

Analytical pyrolysis has been successfully used for monitoring the curing process of certain polyimide polymers. For example, the polyimide Matrimid 5292[®] is obtained from two components in a reaction as shown below:

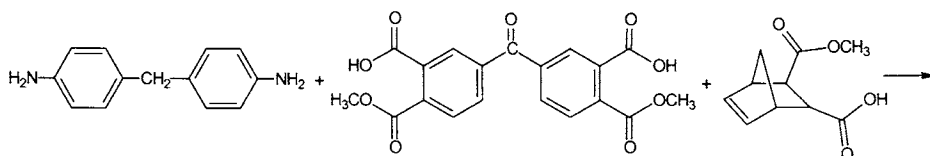


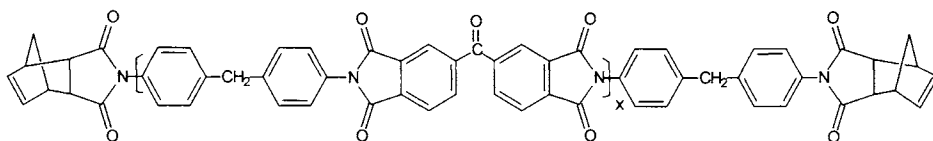
The maleimide end of the polymer further reacts with the condensate and generates a tridimensional material with resistance to high temperatures. The reaction continues as shown below:



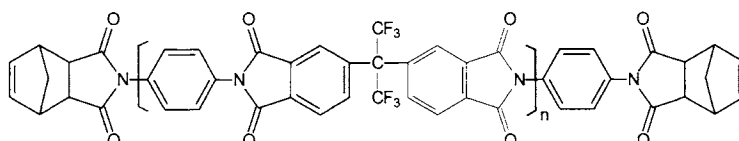
The progress of polymerization of Matrimid 5292[®] can be monitored by Py-GC/MS [19]. The levels of methylphenol, 4-succinimido-4'-aminodiphenylmethane, and 2-(2-propenyl)-4-methylphenol are increased in the pyrolysate as the degree of curing increases. At the same time, the level of 3,3'-diallyl bisphenol A decreases with increasing cure.

Other polyimides also are used in crosslinked resins with high thermal resistance. These compounds are obtained from reactions as shown in an example below:



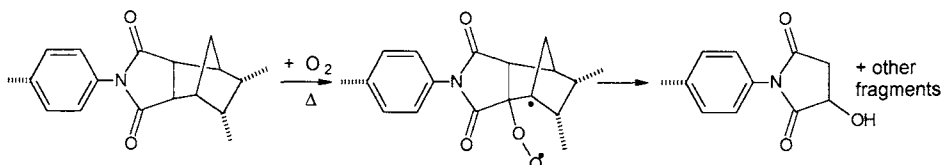


The pre-polymer has a very low DP ($x < 3$). The norbornene-ended polyimide (norbornene-2,3-dicarboxylic imide also known as nadic imide) is further polymerized by heating it at about 300° C. The thermosetting process of norbornene-ended polyimide can be investigated by Py-GC/MS. For example, the crosslinking of norbornene-ended polyimide PMR-II, was investigated using Py-GC/MS [20] (the pre-polymer PAR-II structure is shown below):

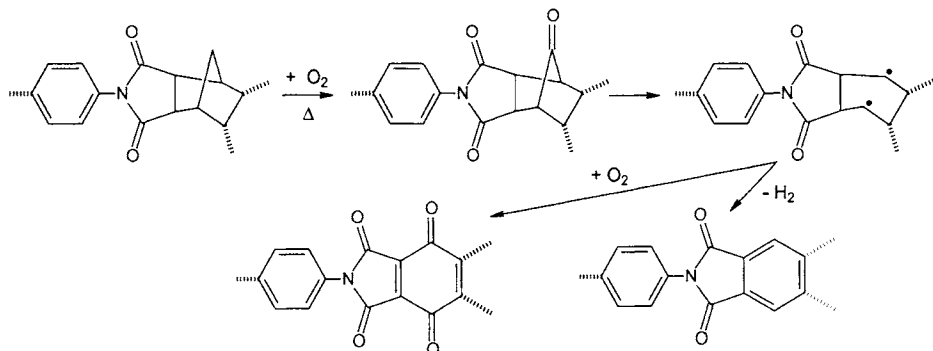


The heating of the pre-polymer between 330° C and 390° C for different periods of time between 2 h and 20 h, leads to different crosslinking levels due to the opening of the terminal groups. The flash pyrolysis at 485° C of the crosslinked materials followed by the monitoring of cyclopentadiene, cyclopentene, and norbornane allows the identification of the extent of crosslinking.

Various other studies on thermal stability of these resins are reported in literature [21–23]. Particular interest was given to the thermooxidative decomposition of these resins. The process occurs by two different paths. One path takes place with depolymerization and significant weight loss:



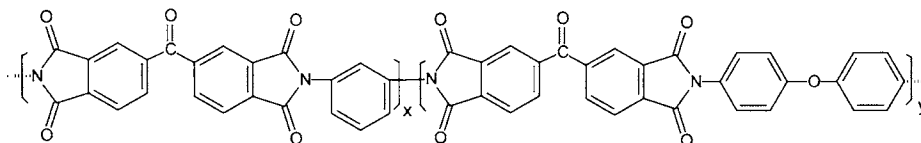
A different path occurs with very little weight loss, leads to more oxidatively stable materials, and keeps the tridimensional structure of the resin. The reactions taking place in this path are shown below:



Attempts were made to modify the end caps such that the thermal or thermooxidative decomposition of the polymer will take place by the second path. For this purpose, various substituents were added at 7-position of the norbornene-2,3-dicarboxylic imide, including OH, SH, F, Cl, allyl, etc. These substituents should not diminish the crosslinking capability of the polymer and favor the second path of thermooxidation. The addition of an OH group, for example, allows crosslinking and offers a promising way to favor the formation of a labile carbonyl in 7-position, such that during oxidation the second path of reaction is followed. The addition of an allyl group provides two double bonds that may be involved in further crosslinking and leads to a different thermal behavior [24].

- Copolymers of imides

Some copolymers of poly(imides) found practical applications, typically due to their good thermal resilience. One such copolymer is poly(3,3',4,4'-benzo-phenone-tetracarboxylic dianhydride-co-*m*-phenylene-4,4'-oxydianiline) with the structure indicated below:



Heated above 550° C the copolymer decomposes and generates CO and CO₂ as well as aromatic compounds [25]. Only a few studies regarding thermal decomposition of these compounds are available. For example, it has been reported that the furfuryl alcohol/formaldehyde resin decomposes in an argon atmosphere at 340–540° C with formation of CO₂ and CO as the main volatile products and with 60% yield of char remaining at 800° C [26, 27].

References 13.4

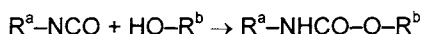
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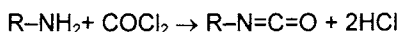
CHAPTER 14

*Poly(urethanes) and Poly(ureas)***14.1 POLY(URETHANES)****- General aspects**

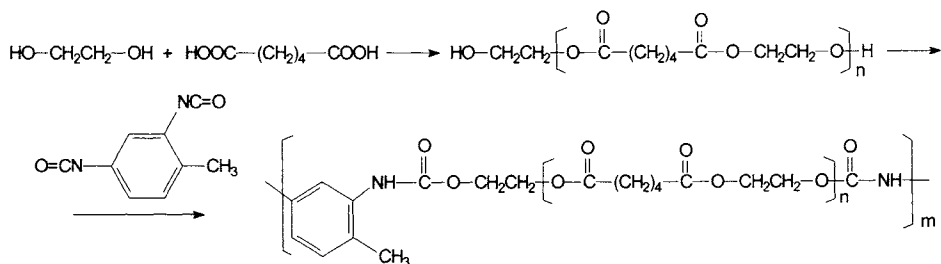
Urethanes (or carbamate esters) are compounds that are the product of the reaction of isocyanates -N=C=O with a hydroxy compound. This reaction can be written as follows:



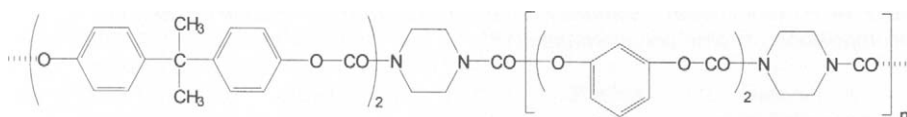
When a diisocyanate reacts with a diol, a linear polyurethane is generated, and when it reacts with a polyol, it generates a cross-linked polymer. The isocyanates are commonly prepared by the reaction of phosgene and primary amines as follows:



The most commonly used diisocyanates are toluene diisocyanate (TDI) (as a mixture of isomers), diphenylmethane *p,p'*-diisocyanate (MDI), naphthylene-1,5-diisocyanate (NDI), hexamethylene diisocyanate (HDI), and isophorone diisocyanate (IPDI). The diol (or the polyol) used in the reaction can be a small molecule, or it can be a low DP polymer with hydroxy end groups. The glycols used in the reaction can be aliphatic diols (glycols), with 1,4-butanediol being most frequently used. The polymeric hydroxy compounds are mainly polyethers, polyesters, or polyester-polyamides with terminal -OH groups. When a polymeric diol is used, the urethane group usually does not constitute the majority of the functional groups within the polyurethane [1, 2]. A typical low DP polymer is made from adipic acid and ethylene glycol and is further reacted with the diisocyanate (such as 1-methyl-2,4-benzene-diisocyanate) as shown below:



The resulting material can be considered a copolymer. Depending on the polyether component, polyurethanes can range from rigid materials to soft elastomers. When alcohols with more than two OH groups are used, a tridimensional crosslinked materials can be obtained. Some of the elastomers can even be vulcanized, depending on their free side groups and the presence of double bonds in the backbone.



Some polyurethanes are used in practice as foams. Foam production is typically performed using polyols with more than three hydroxy groups, which leads to a cross-linked polymer. The reaction is typically base catalyzed by tertiary amines. In order to make a foam, a blowing agent is incorporated in the reaction mixture. This can be a controlled quantity of H_2O . The H_2O reacts with an isocyanate group to form an unstable carbamic acid that decomposes to produce the corresponding amine and CO_2 gas. Volatile liquids such as fluorocarbons can be used as alternative blowing agents.

Since polyurethanes are frequently used in household objects, their thermal degradation and products generated during burning were studied frequently [3–5]. Among these can be included studies on polyester-urethanes [6], polyether-urethanes [7], phenol-formaldehyde urethane [8], studies on the influence of fire retardants on polyurethane decomposition [9, 10], generation of isocyanates during decomposition [11], and other studies [12–17]. Some reports on thermal decomposition of polyurethanes are summarized in Table 14.1.1.

TABLE 14.1.1. Summary regarding literature information on thermal decomposition of some polyurethanes [18].

Polymer	Temp. °C	Results	Ref.
poly(oxy-1,3-phenylene-oxy-carbonyl-imino-1,4-phenylene-methylene-1,4-phenylene-iminocarbonyl)	ambient to 500	1,4-butanediol, methylene bis-(4-phenyl isocyanate), tetrahydrofuran, CO_2 , H_2O , butadiene, HCN, CO	19
poly(oxy-1,3-phenylene-oxy-carbonyl-imino-1,4-phenylene-methylene-1,4-phenylene-iminocarbonyl) + 10% (w/w) ammonium polyphosphate	ambient to 500	methylene-bis-(4-phenyl isocyanate), tetrahydrofuran, H_2O , aniline, formaldehyde, CO_2	20
poly(oxy-1,3-phenylene-oxy-carbonyl-N-methylimino-hexamethylene-N-methyliminocarbonyl)	320	cyclic monomer, dimer and trimer, resorcinol	21, 22
poly(oxy-1,4-phenylene-oxy-carbonyl-N-methylimino-1,4-phenylenemethylene-1,3-phenylene-N-methylimino-carbonyl)	325	cyclic dimer, 4,4'-N-methyldiphenylmethane, hydroquinone, and higher chain fragments	21
poly(oxy-1,4-phenylene-oxy-carbonyl-N-piperazine-1,4-diyl-carbonyl)	360	cyclic dimer and trimer, resorcinol, and various chain fragments	21
poly(oxy-1,4-phenylene-isopropylidene-1,4-phenyleneoxycarbonyl-N-imino-1,4-phenylenemethylene-1,4-phenylene-N-iminocarbonyl)	190	4,4'-diphenylmethane diisocyanate, bisphenol A	23

TABLE 14.1.1 (continued). Summary regarding literature information on thermal decomposition of some polyurethanes [18].

Polymer	Temp. °C	Results	Ref.
poly(oxy-1,4-phenylene-isopropylidene-1,4-phenylene-oxy-carbonyl-N-methylimino-1,4-phenylenemethylene-1,4-phenylene-N-methylimino-carbonyl)	-	bisphenol A, 4,4'-N-methyldiphenyl methane and linear and cyclic fragments of the main chain	23
poly(oxy-1,4-phenylene-isopropylidene-1,4-phenylene-oxy-carbonyl-N-methyl-imino-hexamethylene-N-methyl-iminocarbonyl)	330	cyclic monomer and dimer, and various chain fragments	21
poly(oxy-1,4-phenylene-isopropylidene-1,4-phenylene-oxy-carbonyl-piperazine-1,4-diyl-carbonyl)	330	cyclic dimer, bisphenol A and various chain fragments	21
poly(oxy-2,2-dimethyltrimethylene)-oxy-carbonyl-N-imino-1,4-phenylenemethylene-1,4-phenylene-N-iminocarbonyl)	350	various fragments of the main chain	22
poly(oxy-xylylene-oxy-carbonylimino-xylylene-iminocarbonyl)	300	CO ₂ , <i>trans</i> -1,4-cyclohexane-dimethanol, 4-methylene-cyclohexanemethanol, xylylenediamine	24
polyester urethane from ethylene/propylene glycol adipic acid polyester butanediol and methyl bis-(4-phenylisocyanate)	ambient to 500	modified chain fragments, ethylene, propylene, CO ₂ , ethylene oxide, propylene oxide, acetaldehyde, tetrahydrofuran, H ₂ O, cyclopentanone, ethylene glycol, propylene glycol, adipic anhydride (trace), aniline (trace)	25
polyurethane from 4,4'-methylenebis(phenylisocyanate), poly(butylene adipate) and 1,4-butandiol extender	250–325	two process account for thermal decomposition, one being the dissociation of the urethane linkage, which yields products with isocyanato and hydroxyl end groups (or unsaturated end groups at higher temperatures), and the second being an ester exchange, which produces cyclic oligomers	26
polyurethane from 4,4'-methylenebis(phenylisocyanate), tetramethyleneglycol adipate oligomers and 1,4-cyclohexane dimethanol extender	250–300	urethane linkage cleaves in the first stage, then the polyester segments decompose at higher temperatures to form cyclic ester oligomers	27
polyurethane from butanediol, phenylphosphonic dichloride and methylene bis-(4-phenylisocyanate)	ambient to 500	CO ₂ tetrahydrofuran, dihydrofuran, aniline, p-toluidine, N-phenylpyrrolidine, N-(p-tolyl)pyrrolidine, cyclobutylene-phenyl phosphonate, butanediol, methylene-bis-(4-phenylisocyanate), 4,4'-methylenedianiline	28
polyurethane from diphenylmethane diisocyanate and poly(oxytetramethylene)glycol	550, 750, 950 in air	numerous aromatic compounds starting with one aromatic ring such as benzene, toluene, ethylbenzene, dimethylbenzene, etc. end as high as four aromatic rings (pyrene), also aniline, benzonitrile, phenyl isocyanate, etc.	29
polyurethane from methylene bis(4-phenylisocyanate) 105 parts and propoxylated trimethyl propane 100 parts	600	methane, CO ₂ , ethylene, ethane, H ₂ O, propene, propane, ethanol, isobutene, acrolein, propanal, 2-methyl-1-butene, 2-methylpropanal, 2-butanone, benzene, dihydropyran, 2,2,4-trimethyl-1,3-dioxalane	30

TABLE 14.1.1 (continued). Summary regarding literature information on thermal decomposition of some polyurethanes [18].

Polymer	Temp. °C	Results	Ref.
polyurethane from methylene bis(4-phenylisocyanate) 105 parts and propoxylated trimethyl propane 100 parts	250–350	CO ₂ , propene, some methane and propanal	31
polyurethane from methylene bis(4-phenylisocyanate) 105 parts and propoxylated trimethyl propane 100 parts	350–500	methane, ethane, ethene, propane, propene, ethanal, propanal, diminishing quantities of CO ₂	31
polyurethane from methylene bis(4-phenylisocyanate) 105 parts and propoxylated trimethyl propane 100 parts	500–650	methane (max. rate of production at 600° C), ethane, ethene, propene, ethanal, propanal	31
polyurethane from methylene bis(4-phenylisocyanate) 105 parts and propoxylated trimethyl propane 100 parts	650–800	methane, ethane, ethene, propene, ethanal, propanal	31
polyurethane from polyadipate of 1,4-butandiol or 1,6-hexandiol and diphenylmethane- <i>p,p'</i> -diisocyanate	500, 600, 700, 800, 900	methane, ethane, ethylene, acetylene, propene, propyne, butane, butene, butadiene, butyne, propanenitrile, cyclopentane, cyclopentadiene, methyl-1,4-pentadiene, benzene, cyclopentanone, toluene, other larger molecules	32

The results for a Py-GC/MS analysis of a polyether-urethane are shown in Figure 14.1.1. The compound is poly[4,4'-methylenebis(phenyl isocyanate)-*alt*-butandiol/polytetrahydrofuran], CAS# 9018-04-6. The pyrolysis was done at 600° C in He in conditions similar for other examples previously discussed (see Table 4.2.2).

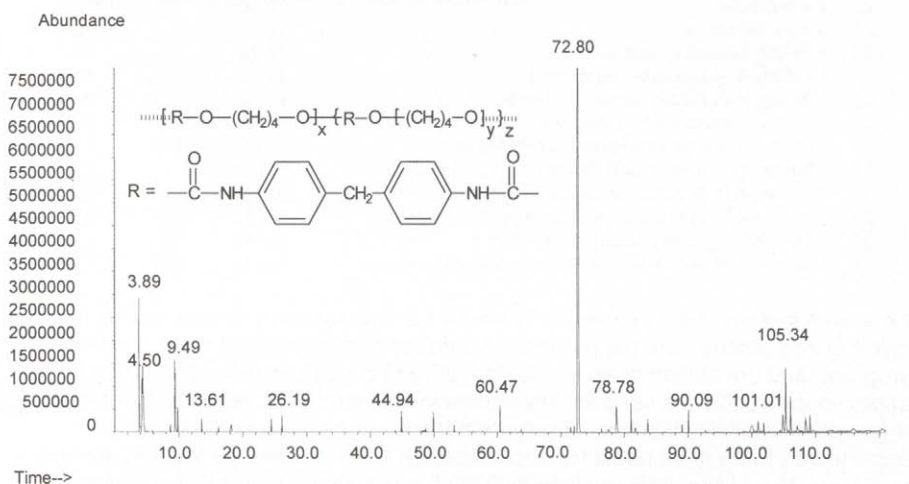


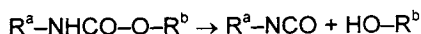
FIGURE 14.1.1. Result for a Py-GC/MS analysis of poly[4,4'-methylenebis(phenyl isocyanate)-*alt*-butandiol/polytetrahydrofuran]. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

The separation was done on a Carbowax column also in similar conditions with other separations and shown in Table 4.2.2. The peak identification for the chromatogram shown in Figure 14.1.1 was done using MS spectral library searches only and is given in Table 14.1.2.

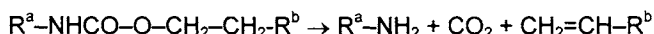
TABLE 14.1.2. Compounds identified in the pyrogram of poly[4,4'-methylenebis(phenyl isocyanate)-alt-butandiol/polytetrahydrofuran] shown in Figure 14.1.1.

Peak	Compound	Ret. time	MW	Area %
1	carbon dioxide	4.34	44	1.15
2	butane	4.50	58	10.49
3	acetaldehyde	5.92	44	trace
4	2,3-dihydrofuran	8.74	70	0.41
5	tetrahydrofuran	9.49	72	4.22
6	butanal	9.90	72	1.32
7	1,1'-oxybisbutane	13.61	130	0.69
8	4-butoxy-1-butene	16.26	128	0.25
9	water	18.27	18	1.05
10	1-butanol	24.49	74	0.66
11	3-buten-1-ol	26.19	72	0.87
12	1-(ethenoxy)butane	44.94	100	1.24
13	tetrahydro-2-methyl-2-furanol	48.71	102	trace
14	1,4-dibutoxybutane	49.98	202	0.99
15	4-but-3-enyloxy-1-butoxybutane	53.22	200	0.31
16	4-butoxy-1-butanol	60.47	146	1.32
17	1-hepten-4-ol ?	63.80	114	trace
18	2-oxepanone	71.57	114	0.32
19	2,6-bis(1,1-dimethylethyl)-4-methylphenol (BHT)	72.12	220	0.34
20	1,4-butandiol	72.80	90	53.73
21	butoxy derivative	76.44		trace
22	4-(4-butoxybutoxy)butanol	78.78	218	2.57
23	1-butoxy-4-(4-butoxybutoxy)butane	81.06	274	1.58
24	1-butoxy-4-(4-butoxybutoxy)but-3-ene	83.72	272	0.65
25	4-(4-but-3-enyloxybutoxy)butanol	89.08	216	0.60
26	1-[4-(4-but-3-enyloxybutoxy)butoxy]but-3-ene	90.09	270	1.21
27	unknown [71(100), 43(22), 98(19), 55(12), 41(12)]	104.86		2.18
28	1-butoxy-4-[4-(4-butoxybutoxy)butoxy]butane	105.34	346	5.91
29	1-butoxy-4-[4-(4-but-3-enyloxybutoxy)butoxy]butane	106.10	344	3.05
30	4-[4-(4-butoxybutoxy)butoxy]butan-1-ol	108.46	290	1.53
31	1-butoxy-4-[4-(4-but-3-enyloxybutoxy)butoxy]but-3-ene	109.15	342	1.35

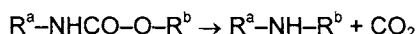
The analysis of pyrolysate shown in Table 14.1.2 indicates only derivatives for the polyether sequences from the polymer. No traces of methylaniline were seen in the pyrogram, and the elution of an amino derivative of benzylbenzene is not likely to happen in the conditions used for this separation. Therefore, the use of pyrolysis results for the identification of this type of polyurethane is not conclusive. At lower temperatures three main paths for decomposition were indicated. One first process is the dissociation of the urethane linkage, taking place as the reverse of urethane formation, as shown below:



Another process is dissociation to a primary amine, an olefin, and carbon dioxide:



The third process is elimination of CO₂ and formation of a secondary amine as follows:



For the case of polyester-polyurethane, the ester linkages are cleaved in a second stage, after the decomposition of the urethane group. The proportion of each individual reaction depends on the nature of the polyurethane, and not all the expected molecular fragments are found in the pyrolysate. Even more, some studies noticed the complete lack of diisocyanate related fragments. This was, for example, the case of pyrolysis of poly[4,4'-methylenebis(phenyl isocyanate)-*alt*-butandiol/ polytetrahydrofuran] given in Figure 14.1.1 and of a few other literature reports [16, 33]. On the other hand, only the presence of diisocyanate moiety and the absence of the polyol related fragments were reported in a different study [34].

In a study done on nine polyester polyurethanes made with relatively close proportions of isocyanate and polyol component, both the diisocyanate and the polyester with diol terminal groups generated by pyrolysis identifiable fragment molecules [4]. The polyurethanes were made using toluene diisocyanate (TDI) (as a mixture of isomers), diphenylmethane *p,p'*-diisocyanate (MDI), hexamethylene diisocyanate (HDI), and isophorone diisocyanate (IPDI), in combination with poly(1,4-butandiol adipate) (PBA), poly(1,6-hexandiol adipate) (PHA) and poly(diethyleneglycol adipate) (PDEA). The polyurethanes included four PBA-TDI polymers with different proportion of TDI varying between 8 wt% and 35 wt%, PBA-IPDI (17% IPDI), PBA-HDI (11% HDI), PBA-MDI (20% MDI), PHA-MDI (22% MDI) and PDEA-MDI (12% MDI). Depending on the polymer, fragments from the adipic acid, the diol, the diisocyanate, and from the ester linkage, were detected in the pyrograms. Toluene diisocyanate itself was a common compound in the polyurethanes made with TDI, and HDI, IPDI, and MDI were detected in the corresponding polyurethanes. The formation of these compounds can even be used for the evaluation of the content of diisocyanate in the polyurethane.

References 14.1

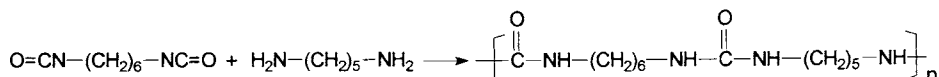
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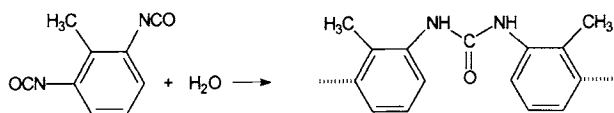
14.2 POLY(UREAS)

- General aspects

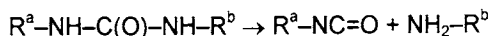
Poly(ureas) can be generated from the reaction of a diisocyanate with a diamine in a step reaction as follows:



Also, the hydrolysis of the isocyanate group can generate ureas. For example, toluene diisocyanate and water will form a polyurea by the following reaction:



Thermal decomposition of these polymers at lower temperatures occurs by the following scheme [1–3]:



For example, pyrolysis of the polyurea generated from the hydrolysis of toluene diisocyanate generated the monomer, diaminotoluene and aminoisocyanatotoluene [4]. At higher temperatures, polyureas generate NH_3 , CO_2 , HCN , CH_4 , some CO , and molecules related to the hydrocarbon moiety from the polymer.

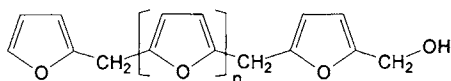
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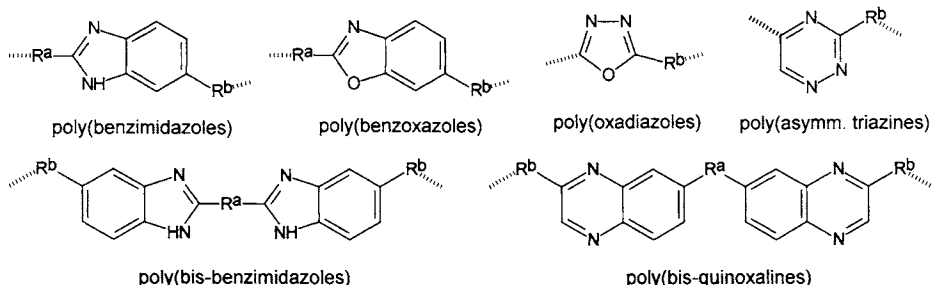
CHAPTER 15

*Polymers Containing Heterocycles in the Backbone***15.1 POLYMERS WITH VARIOUS HETEROCYCLES IN THE MAIN CHAIN****- General aspects**

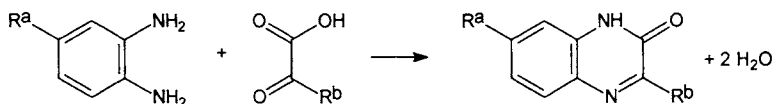
The diversity of polymers containing heterocyclic groups is quite large. These polymers may include macromolecules generated from the polymerization of a unique monomer, such as poly(furfuryl alcohol), CAS# 25212-86-6, with the formula shown below:



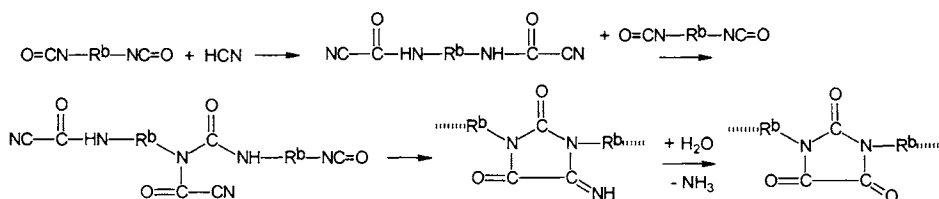
or they may include bi- or poly-functional heterocyclic groups together with aromatic and/or aliphatic fragments. The result is that some polymers from this class have a simple and uniform composition, such as poly(thiophene-2,5-diyl). Other polymers may have a more complicated structure. Among these are poly(quinoxalines), poly(benzimidazoles), poly(benzoxazoles), poly(oxadiazoles), poly(triazines), etc. A number of imides containing a pyrroline-2,5-dione ring (maleimide) also can be considered as macromolecules containing heterocycles. However, these polymers were included in the class of imides and were discussed in Section 13.4. Examples of polymers with heterocycles in their structures (not including maleimide polymers) are shown below:



where R^a is nought, CH_2 , O, phenylene, etc. and R^b is phenylene, oxydiphenyl, or more complicated fragments. These polymers are synthesized by different procedures, such as condensations of the type:

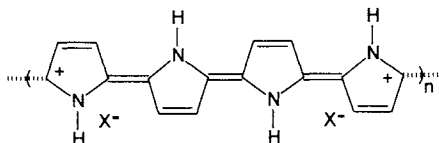


which leads to 1,2-dihydroquinoxalin-2-one derivatives. Other polymers are generated by reactions in more steps, such as the derivatives of poly(parabanic acid), which can be obtained by the following chain of reactions:



Some polymers containing heterocycles can be included in resins following further condensation. This is possible, for example, for poly(furfuryl alcohol), which can condense with formaldehyde, phenol, melamine and urea. Furfuryl alcohol-formaldehyde copolymer can be synthesized in the reaction of furfuryl alcohol with formaldehyde in the presence of oxalic acid as catalyst.

Depending on their structure, the polymers containing heterocycles have various applications. For example, poly(furfuryl alcohol) is used in composite materials with fillers such as sand and concrete, in copolymers with formaldehyde, etc. Some of the polymers from this group have special properties such as good electrical conductivity (after appropriate doping). Among these polymers are poly(thiophene-2,5-diyl) and particularly polypyrrole, CAS# 109-97-7, (usually in carbon black doped with an organic acid anion). The structure of this polymer is shown below:



X^- = organic sulfonic acid dopant anion

The increase in the size of the units from the polymeric backbone was shown to diminish the flexibility of the macromolecular chain, which has as a result an increase in the melting point. The increase in the melting point of a polymer is paralleled by the increase in its thermal stability. Stiffening the polymeric chain by the inclusion of ring structures, possibly with fused-ring groups, leads to the polymers with higher thermal stability. Typical ring systems that have been introduced into polymer chains (as diyl groups) include benzene, diazine, triazine, triazole, thiazole, oxadiazole, isoindoline-1,3-dione, 3-pyrrolino[3,4-f]isoindoline-1,3,5,7-tetraone, etc. Also, multiple bonds in the backbone, as in ladder polymers, increase thermal stability (see Section 3.1). Following these ideas a series of polymers with heterocyclic groups were synthesized, leading to good thermal resistance. A few examples are shown in Table 15.1.1.

TABLE 15.1.1. *Polymers with elevated decomposition temperature containing heterocycles in the backbone.*

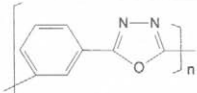
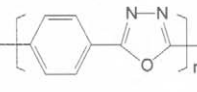
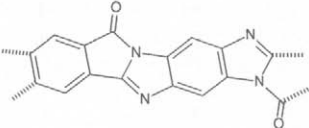
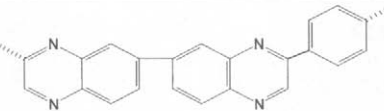
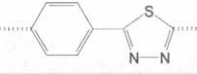
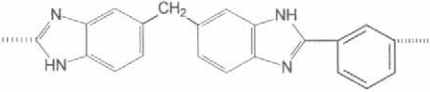
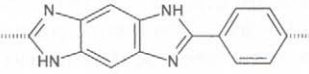
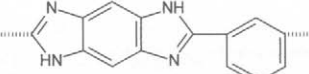
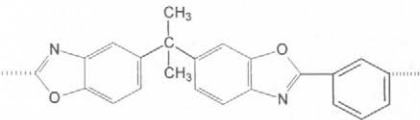
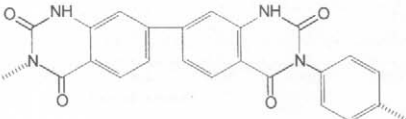
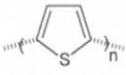
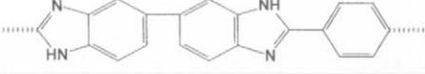
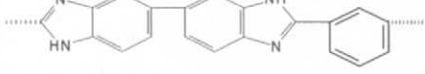
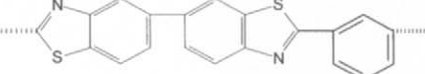
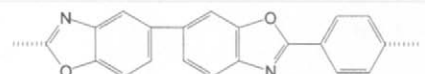
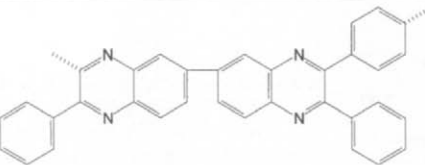
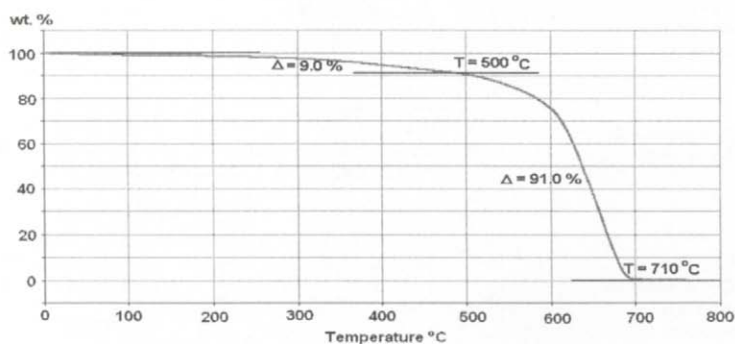
Polymer	Structure	Decomposition temperature °C
poly(<i>m</i> -phenylene-1,3,4-oxadiazole) CAS# 26100-80-1		400
poly(<i>p</i> -phenylene-1,3,4-oxadiazole) CAS# 26023-46-1		450
poly(benz-imidazopyrrone)		450
poly(6,6'-bisquinoxalin-3,3'-diyl-1,4-phenylene)		470
poly(1,4-phenylene-2,5-thiadiazolyl)		490
poly(5,5'-bibenzimidazolylmethane-2,2'-diyl-1,3-phenylene)		490
poly(2,6- <i>p</i> -phenylenedi-imidazobenzene)		500
poly(2,6- <i>m</i> -phenylenedi-imidazobenzene)		500
poly(2,2'- <i>m</i> -phenylene-2,2-bibenzoxazol-5',5'-yl-2-propane)		500
poly(1,1',2,2',3,3',4,4'-octahydro-2,2',4,4'-tetraoxo-3,3'- <i>p</i> -phenylene-6,6'-biquinazolinyl)		540

TABLE 15.1.1 (continued). *Polymers with elevated decomposition temperature containing heterocycles in the backbone.*

Polymer	Structure	Decomposition temperature °C
poly(thiophene-2,5-diyl)		550
poly(5,5'-bibenzimidazolyl-2,2'-diyl-1,4-phenylene)		550
poly(5,5'-bibenzimidazolyl-2,2'-diyl-1,3-phenylene)		550
poly(5,5'-bibenzothiazol-2,2'-diyl-1,3-phenylene)		550
poly(5,5'-bibenzoxazole-2,2'-diyl-1,4-phenylene)		550
poly[6,6'-bis(2-phenylquinoxalin-3,3'-diyl)-1,4-phenylene]		600

An example of a TGA curve for one polymer with high decomposition temperature is given for poly(thiophene-2,5-diyl). The thermogram is shown in Figure 15.1.1, and was obtained using heating in air between 30° C and 830° C at a rate of 10° C/min.

FIGURE 15.1.1. *Variation of weight % loss for poly(thiophene-2,5-diyl) in a TGA experiment at a heating rate of 10° C/min.*

The TGA shows that the polymer starts to lose some weight around 400° C, and the decomposition accelerates above 500° C. Volatile product may include H₂S (see flash pyrolysis results) and oxidation products such as SO₂.

- Homopolymers and alt-copolymers containing heterocyclic groups

The thermal decomposition of the polymers containing heterocyclic groups was studied frequently for practical purposes [1–3]. A number of polymers from this class, having good thermal stability, are used in applications such as preparation of adhesives with high temperature resistance, manufacturing of high performance composites used in the aerospace industry, etc. Other polymers are used in photolithographic industry. Some of the thermal stability studies on polymers containing heterocyclic groups, as reported in literature, are summarized in Table 15.1.2 [4].

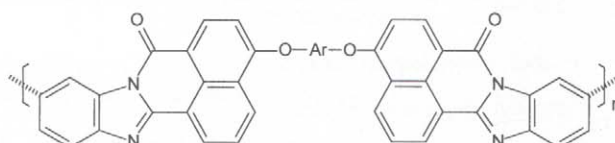
TABLE 15.1.2. Summary regarding literature information on thermal decomposition of polymers containing heterocyclic groups [4].

Polymer	Temp. °C	Results	Ref.
furfuryl alcohol resin (cured with alcoholic ZnCl ₂ soln.)	340-540	CO ₂ and CO; activation energy of decomposition 92.9 kJ mol ⁻¹ , char yield 60% at 800 °C	5, 6
poly(1-methylene-2-imidazolidinone)	240	formaldehyde (trace)	7
poly(3,4-ethylene-dioxythiophene)	390-450	structure degradation	8
poly[3-(4-octylphenyl)-2,2'-bithiophene]	800	H ₂ S, COS, SO ₂ , CH ₃ SH, CS ₂ , S ₈ , C ₁ -C ₈ alkanes and alkenes, benzene, ethylbenzene, toluene, styrene, octylbenzene, thiophene, methylthiophene, bithiophene	9
poly[3-(4-octylphenyl)-thiophene]	550-1400	C ₁ -C ₈ alkanes and alkenes, H ₂ S, CS ₂ , benzene, toluene	9
poly(3-octyl-2,2'-bithiophene)	550-1400	C ₁ -C ₈ alkanes and alkenes, H ₂ S, CS ₂ , benzene, toluene	9
poly(3-octylthiophene)	550-1400	C ₁ -C ₈ alkanes and alkenes, H ₂ S, CS ₂ , benzene, toluene	9
poly(5,5'-bibenzimidazole-2,2'-diyl-1,3-phenylene)	599-667	gaseous products; H ₂ , NH ₃ , HCN, and CH ₄ ; products nonvolatile at ambient temperature after approx. 50% weight loss; benzimidazole (29.8%), benzoxazole (4.9%), 2-methylbenzimidazole (7.3%), 2-phenylbenzimidazole (24.3%), 2-(3-methylphenyl)benzimidazole (5.3%), 5-(3-aminophenyl)-benzimidazole (9.6%), 2-(3-cyanophenyl)-benzimidazole (7.8%), 5,5'-bibenzimidazole (4.4%), 2-phenyl-5-(3-aminophenyl)benzimidazole (4.4%), 2-phenyl-5,5'-bibenzimidazole (1.9%), 2-phenyl-5-(benzoxazole)benzimidazole (0.3%)	10
poly(5,5'-bibenzimidazole-2,2'-diyl-1,4-phenylene)	400-700	phenol, terephthalodinitrile, benzonitrile, 4,4'-diaminodiphenyl, H ₂ , CO, NH ₃ , HCN, traces of aniline, carbonaceous residue	11
poly(5,5'-bibenzimidazole-2,2'-diyl-1,4-phenylene)	570, 700, 1000	H ₂ (700 and 1000° C), NH ₃ (570 and 700° C), N ₂ O, HCN, cyanogen (570° C only), CH ₄ , C ₂ H ₆ , ethylene, acetylene (700 and 1000° C), acetonitrile (700 and 1000° C), propene (570 and 700° C), benzene, toluene, benzonitrile (700° C only), ethylbenzene, methylbenzonitrile (700° C only)	12
poly(parabanic acid-alt-diphenylmethane)		CO ₂ , CO, NO, phenyl isocyanate	13, 14
poly(parabanic acid-alt-diphenyl ether)		CO ₂ , CO, NO, isocyanates	13, 14
poly(perfluoropyridine)		volatiles comprise CO ₂ , CO, SiF ₄ (all from silica vessel); carbonaceous residue	15
poly(thiophene)	400	weight loss, char residue in reducing atmosphere	16

TABLE 15.1.2 (continued). Summary regarding literature information on thermal decomposition of polymers containing heterocyclic groups [4].

Polymer	Temp. °C	Results	Ref.
poly{5,5'-carbonylbis[1,3-isobenzofurandione]- <i>alt</i> -bis(3-aminophenyl-methanone)}	550	10% weight loss in air	17
polypyrrole (20 wt %) in carbon black doped with an organic acid anion	600-800	pyrrole, SO ₂ from the counterion	18
polyquinolines and polyquinoxalines	800	various fragments	19

Polymers with a higher number of bonds along the backbone (pseudo ladder), which have good heat resistance, also were synthesized and studied by pyrolytic techniques. Among these were several poly[aryl ethers of bis(benzimidazobenzisoquinolinones)] with the structure indicated below:



where Ar represents an aromatic moiety. Pyrolysis at 650° C of several such polymers generated specific small molecules. For example, for Ar = 1,4-penylene the pyrolysate contained phenol; for Ar = 1,3-phenylene the pyrolysate contained phenol and resorcinol; for Ar = 4,4'-biphenyl the pyrolysate contained 4-phenylphenol and 4,4'-bisphenol; for Ar = 2,7-naphthalene the pyrolysate contained 2-naphthol, 2,7-dihydroxynaphthalene, and naphthalene; for Ar = bis(4-phenylene) ketone the pyrolysate contained phenol and CO₂; for Ar = bis(4-phenylene) sulfone the pyrolysate contained phenol and SO₂; for Ar = bis(4-phenylene)isopropane the pyrolysate contained phenol, isopropylphenol, and propane; for Ar = bis(4-phenylene)fluorene the pyrolysate contained phenol, fluorene, and phenylfluorene; and for Ar = bis(4-phenylene) sulfide the pyrolysate contained phenol, H₂S, and thiophenol [20].

Thermal properties of some other polymers containing heterocycles are reported in literature. For example, the polymers containing triazine networks substituted with perfluoro-*n*-propyl or perfluoroalkyloxy groups do not decompose easily upon heating. These types of polymers are used as heat resistant oils, and several studies on their thermal decomposition are available in literature [21–23].

The results for a Py-GC/MS analysis of poly(thiophene-2,5-diyl) Br terminated, CAS # 110-02-1, are shown in Figure 15.1.2. Since the polymer is rather resistant to heat, pyrolysis was done at 850° C in He. Other conditions were kept similar to those for other examples previously described (see Table 4.2.2). The heating rate was kept 20° C/ms and THT 10 s. The separation was done on a Carbowax column (60 m, 0.32 mm i.d., 0.32 μm film thickness) with the GC starting at 40° C with a ramp of 2° C/min. up to 240° C and a final oven time of 20 min. The MS was operated in EI+ mode. The peak

identification was done using MS spectral library searches only and is given in Table 15.1.3.

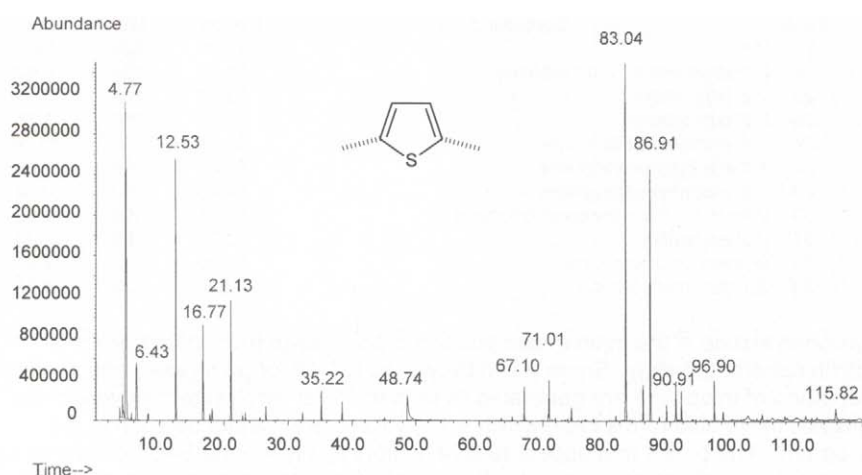


FIGURE 15.1.2. Pyrogram from a Py-GC/MS analysis of a poly(thiophene-2,5-diyl) Br terminated sample. Pyrolysis done on 0.4 mg material at 850° C in He, with the separation on a Carbowax type column.

TABLE 15.1.3. Compounds identified in the pyrogram of a poly(thiophene-2,5-diyl) Br terminated sample as shown in Figure 15.1.2.

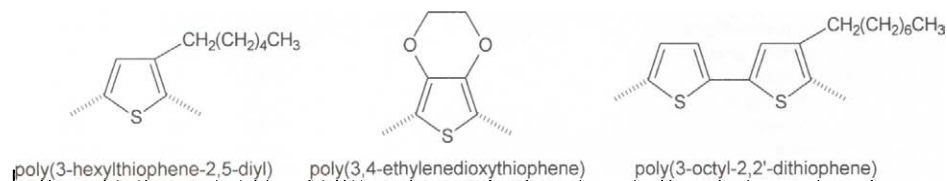
Peak	Compound	Ret. time	MW	Area %
1	hydrogen sulfide	4.77	34	26.04
2	bromomethane	5.65	94	trace
3	carbon disulfide	6.43	76	4.94
4	benzene	12.53	78	10.20
5	thiophene	16.77	84	4.78
6	toluene	17.82	92	trace
7	water	18.19	18	0.68
8	2-methylthiophene	21.13	98	4.98
9	3-methylthiophene	22.91	98	trace
10	ethylbenzene	23.36	106	trace
11	3,4-dimethylthiophene	25.63	112	trace
12	2-ethylthiophene	26.57	112	0.65
13	styrene	32.29	104	trace
14	2-vinylthiophene	35.22	110	1.20
15	bromobenzene	38.49	156	0.83
16	2-(2-methylvinyl)thiophene	45.11	124	trace
17	benzenethiol	48.74	110	3.34
18	naphthalene	63.48	128	trace
19	1-(2-thienyl)ethanone	65.19	126	trace
20	benzo[b]thiophene	67.10	134	1.51
21	2-methylbenzo[b]thiophene	70.84	148	trace
22	thieno[3,2-b]thiophene	71.01	140	2.22

TABLE 15.1.3 (continued). Compounds identified in the pyrogram of a poly(thiophene-2,5-diyl) Br terminated sample as shown in Figure 15.1.2.

Peak	Compound	Ret. time	MW	Area %
23	BHT	71.96	220	trace
24	2-methylthieno[3,2-b]thiophene	74.52	154	0.62
25	2,2'-bithiophene	83.04	166	17.40
26	2,3'-bithiophene	85.77	166	1.71
27	2,2'-methylenedithiophene	86.91	180	11.54
28	2,3'-methylenedithiophene	88.28	180	trace
29	3,3'-methylenedithiophene	89.43	180	0.74
30	2-methyl-2,2'-methylenedithiophene	90.91	194	2.09
31	diphenylsulfide	91.77	186	1.33
32	2-phenylthiophene	96.90	192	2.01
33	2,7-dibromofluorene ?	115.82	322	1.18

Hydrogen sulfide is the main decomposition product seen from the pyrolysis of poly(thiophene-2,5-diyl). Some 2,2'-bithiophene (17.4% of pyrolysate) and only a small proportion of thiophene are generated (less than 5% of pyrolysate). However, the pyrolysis in He also forms char, which is not volatile and cannot be seen in the pyrogram. The bonds that appear to cleave more easily are the S–C bonds and the bonds between the thiophene units (C–C type). Since the hydrogen content of the polymer is low, the formation of SH₂ is associated with the formation of char. The elimination of some carbon and sulfur as CS₂ or S_x explains the formation of benzene, thiophene, etc.

Mechanical properties of poly(thiophene-2,5-diyl) are not suitable for many practical uses. Polymers with higher flexibility and still good thermal resistance or with other special conductivity properties (after doping) can be obtained from the polymerization of substituted polythiophenes. Some examples are shown below:



Thermal decomposition of poly(3-hexylthiophene-2,5-diyl) is described by its TGA curve shown in Figure 15.1.3. The thermogram was obtained from a sample with M_w = 87,000 in air, by heating between 30° C and 830° C at a rate of 10° C/min.

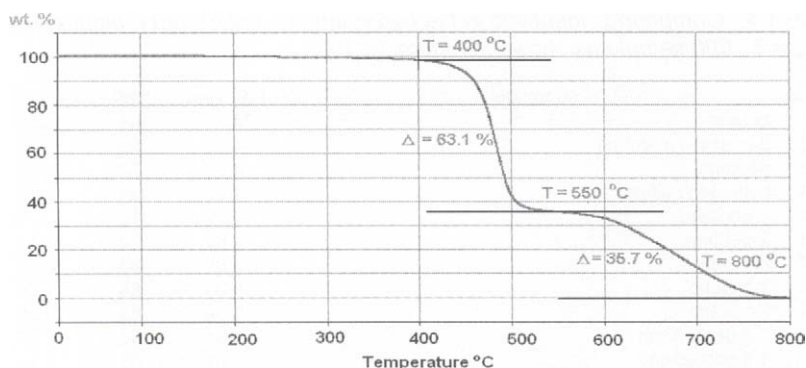


FIGURE 15.1.3. Variation of weight % loss for poly(3-hexylthiophene-2,5-diyl) $M_w = 87,000$ in a TGA experiment at a heating rate of 10°C/min .

The hexyl groups represent about 50% of the weight of the polymer. However, the weight loss between 400°C and 500°C is larger than 50%, indicating that the structure of the polymer is affected by heat not only through the elimination of the side chain groups, but also including the backbone modification. The char remaining at temperatures higher than 500°C is oxidized in air with formation of oxides of carbon and sulfur.

The results for a Py-GC/MS analysis of a poly(3-hexylthiophene-2,5-diyl) sample, CAS # 104934-50-1, (regioregular) with $M_w = 87,000$ are shown in Figure 15.1.4. Since the polymer is rather resistant to heat, pyrolysis was done at 850°C in He. Other conditions were kept similar to those for other examples previously described (see Table 4.2.2). The separation was done on a Carbowax column. The peak identification was done using MS spectral library searches only and is given in Table 15.1.4.

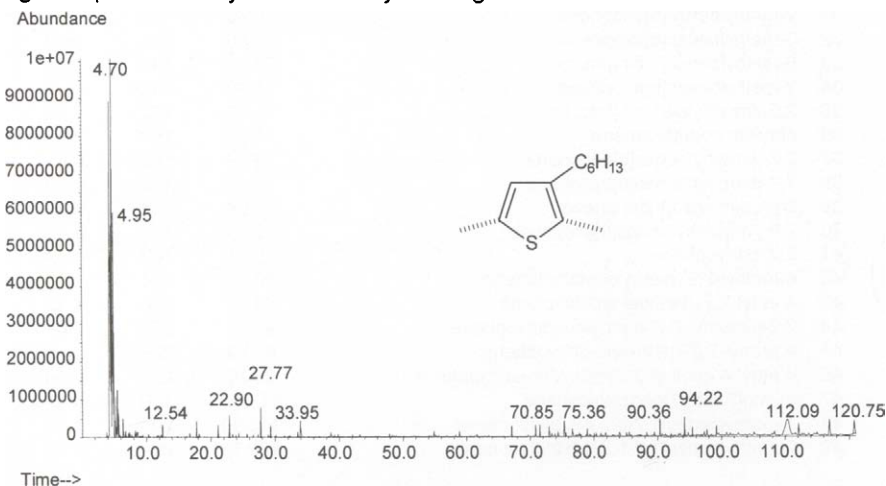


FIGURE 15.1.4. Pyrogram from a Py-GC/MS analysis of a poly(3-hexylthiophene-2,5-diyl) sample, regioregular, $M_w = 87,000$. Pyrolysis done on 0.4 mg material at 850°C in He, with the separation on a Carbowax type column.

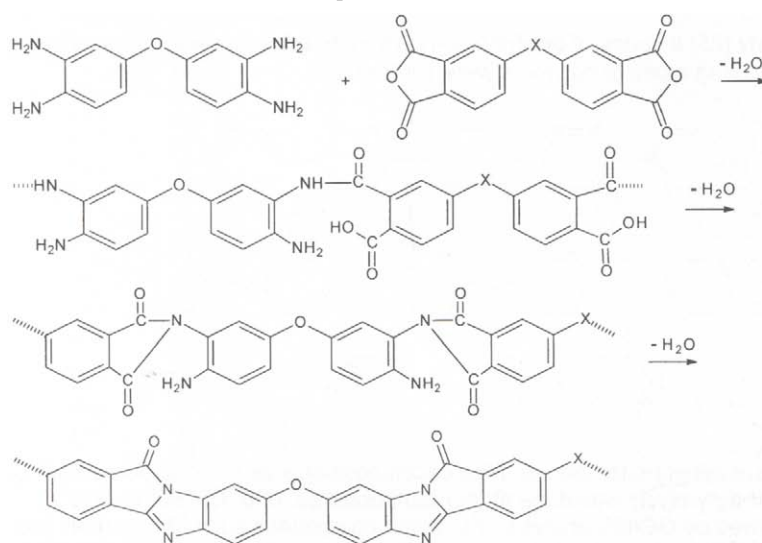
TABLE 15.1.4. Compounds identified in the pyrogram of a poly(3-hexylthiophene-2,5-diyl), $M_w = 87,000$ sample as shown in Figure 15.1.4.

Peak	Compound	Ret. Time	MW	Area %
1	butane	4.39	58	22.49
2	2-methyl-1-propene	4.46	56	6.35
3	pentane	4.57	72	7.97
4	hydrogen sulfide	4.67	34	3.73
5	1-pentene	4.70	70	13.74
6	2-pentene	4.80	70	5.13
7	hexane	4.95	86	8.35
8	1-hexene	5.26	84	1.56
9	2-hexene	5.38	84	0.35
10	1,3-pentadiene	5.54	68	2.29
11	1,4-pentadiene	5.71	68	1.13
12	1-heptene	6.40	98	1.13
13	cyclopentadiene	6.46	66	trace
14	cyclohexadiene	8.33	80	trace
15	benzene	12.54	78	0.70
16	thiophene	16.77	84	trace
17	toluene	17.81	92	0.83
18	2-methylthiophene	21.12	98	0.63
19	3-methylthiophene	22.90	98	1.13
20	3,4-dimethylthiophene	25.63	112	trace
21	2-ethylthiophene	26.57	112	trace
22	2,4-dimethylthiophene	27.77	112	1.57
23	2,3-dimethylthiophene	29.28	112	0.63
24	2-ethyl-5methylthiophene	33.53	126	trace
25	2,3,4-trimethylthiophene	33.95	126	0.98
26	3,4-diethylthiophene	38.68	140	trace
27	methylvinylthiophene	42.08	124	trace
28	methylvinylthiophene	43.26	124	trace
29	hexylthiophene	54.84	168	trace
30	benzo[b]thiophene	67.10	134	0.64
31	2-methylbenzo[b]thiophene	70.85	148	0.67
32	3-methylbenzo[b]thiophene	71.50	148	0.72
33	6-methylbenzo[b]thiophene	72.97	148	0.78
34	?-methylbenzo[b]thiophene	73.40	148	trace
35	2,5-dimethylbenzo[b]thiophene	75.36	162	0.93
36	ethylbenzo[b]thiophene	75.57	162	trace
37	2,7-dimethylbenzo[b]thiophene	76.59	162	trace
38	?,?-dimethylbenzo[b]thiophene	78.96	162	trace
39	2-propylbenzo[b]thiophene	81.84	176	trace
40	2,5,7-trimethylbenzo[b]thiophene	83.99	176	trace
41	2,3'-bithiophene	85.77	166	trace
42	4-methyl-2,2'-methylenedithiophene	90.36	194	1.06
43	4-ethyl-2,2'-methylenedithiophene	94.22	208	1.12
44	?,?-dimethyl-2,2'-methylenedithiophene	95.44	208	0.51
45	4-propyl-2,2'-methylenedithiophene	97.74	222	trace
46	4-ethyl-4'-methyl-2,2'-methylenedithiophene	99.20	222	0.54
47	thieno[3,2-b][1]benzothiophene	112.09	190	1.11
48	1-methylbenzo[1,2-b:3,4-b']dithiophene	116.90	204	1.77
49	2-methylbenzo[1,2-b:3,4-b']dithiophene	120.75	204	1.71

As seen from the pyrogram and from the pyrolysate composition shown in Table 15.1.4, the main components are generated from the hexyl side chain. Some other pyrolysis

products are similar to those for poly(thiophene-2,5-diyl). Char is also formed in the pyrolysis of this polymer.

Among the heterocyclic compounds that were studied by Py-GC/MS are also a number of polybenzimidazopyrrolones [24]. The synthesis of these compounds has been achieved based on the following reactions:



where X is a polymer extender. The nature of this extender X influences considerably the composition of the pyrolysate, obtained at 950°C with a pyrolysis time of 7 s. The pyrolysate composition is shown in Table 15.1.5

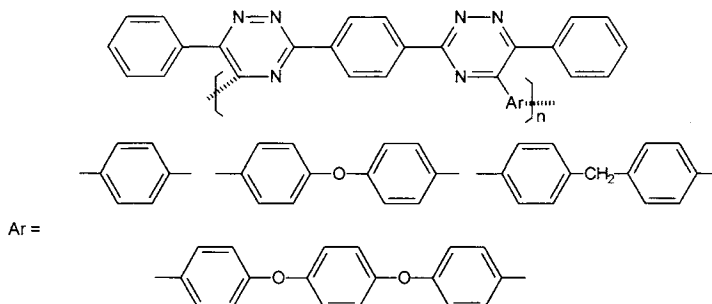
TABLE 15.1.5. The list of compounds identified in the pyrolysate of polybenzimidazopyrrolones with different extenders X and their Area % in the pyrogram [24]

Compound	MW	Area % for various extenders X							
		(CF ₃) ₂	SO ₂	CO	O	A*	nought	B*	C*
carbon dioxide	44	5.74	18.65	24.51	25.11	6.92	26.27	43.64	53.35
hydrogen cyanide	27	36.58	18.93	21.18	19.29	3.93	32.87	6.79	4.33
acetonitrile	41	2.47	7.38	4.49	3.86	0.73	5.55	2.37	1.53
benzene	78	trace	8.11	6.16	4.60	2.47	5.88	11.65	10.10
toluene	92	trace	0.92	0.38	0.34	0.19	trace	3.48	6.91
dimethylacetamide	87	7.04	2.35	7.31	5.56	trace	1.06	0.24	0.87
phenol	94	3.50	2.70	3.30	7.51	64.30	1.76	0.20	0.38
phenylamine	93	absent	1.30	1.22	1.95	0.50	1.63	2.04	1.71
benzonitrile	103	1.04	17.43	12.53	6.80	1.38	8.72	12.30	5.65
methylphenylnitrile	117	absent	absent	absent	absent	absent	absent	3.10	4.75
4-aminobenzonitrile	118	1.48	trace	1.02	2.09	1.23	0.62	0.88	0.39
1,4-dicyanobenzene	128	3.10	1.58	trace	6.26	1.38	absent	0.89	0.49
biphenyl	154	1.69	trace	trace	3.99	1.06	0.51	1.25	0.20
benzimidazole	118	1.63	5.75	2.70	trace	0.82	0.38	0.69	0.47
1,3-isoxindoleione	147	1.60	6.77	1.78	2.46	1.21	3.09	1.14	3.36
benzophenone	182	absent	trace	absent	trace	0.77	absent	0.57	0.89
2-phenylbenzimidazole	194	1.72	absent	trace	3.59	8.59	0.90	4.10	absent

* A = O-C₆H₄-O, B = Si(CH₃)₂, C = Si(CH₃)₂-O-Si-(CH₃)₂

The results shown in Table 15.1.5 indicate that a considerable proportion of bond cleavage occurs at the extender connection, and also that the extender influences the thermal stability of the polymer. Regarding the decomposition of the heterocyclic moiety, the ether bond between the two isoindolino[2,1-a]benzimidazol-11-one units and the C(O)–N bond from the pyrrolydin-2-one ring are likely to cleave more easily than other parts of the molecule.

In a different study [25] a series of poly[phenyl-(asymm. triazines)] were analyzed by Py-GC/MS. The following types of polymers were synthesized:



The polymers were resistant to heat, and the decomposition was minimal below 600° C. For this reason, the pyrolysis was done at four temperatures, 650° C, 750° C, 850° C, and 950° C, followed by GC/MS analysis. For some compounds such as benzene, the yield in the pyrolysate increased as temperature increased, but for other compounds, either the yield had a maximum in the range or even slightly decreased. Among the compounds determined in the pyrolysate were some common for all polymers such as benzene, benzonitrile, benzylamine, 1,4-benzenedicarbonitrile, and phenanthridine. Other compounds in the pyrolysate were specific for the aromatic extender Ar. Among these were 1H-benzotriazole, 1-phenylphthalazine, 9-anthracenecarbonitrile, α -aminobenzeneacetonitrile, 4-phenoxybenzonitrile, 4,4'-oxydibenzonitrile, 1-hydroxy-4-phenoxybenzonitrile, 4-benzylphenylcarbonitrile, 4-phenoxy-4'-phenoxybenzonitrile etc. The degradation mechanism of these polymers starts with a random homolytic cleavage of the N–N and C–N bonds in the triazine ring. This leads to the formation of benzonitrile radicals and p-dicyanobenzene radicals that further propagate the decomposition. The termination occurs with various recombinations and rearrangements.

- Copolymers containing heterocyclic groups

Several copolymers with heterocycles studied using pyrolytic techniques include poly[pyrrole-graft-(2-N-pyrrolyl)ethylvinylether] [26] and several polypyrrole/polytetrahydrofuran graft copolymers including pyrrole ended-polytetrahydrofuran, p-toluene sulfonate doped polypyrrole, and p-toluene sulfonate doped polypyrrole-co-polytetrahydrofuran [27]. The data showed that pyrrole ended-polytetrahydrofuran degrades via mixed random cleavage and unzipping mechanism followed by hydrogen transfer reactions. Cleavage of the pyrrole ring and a lack of high mass fragments are noticed for the doped polymers.

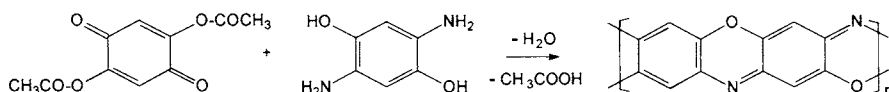
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15.2 LADDER TYPE POLYMERS WITH HETEROCYCLIC STRUCTURE

- General aspects

Ladder polymers have their backbone made from an interrupted series of condensed rings. In such polymers, very frequently the rings contain heteroatoms, and the polymer can be considered as part of the class of polymers with heterocycles in the main chain. One of the first synthesized polymers from this class was obtained from the oxidation and heating of polyacrylonitrile [1, 2]. Multifunctional condensations also can lead to ladder polymers. For example, a poly(phenoxazine) is formed from the reaction of a substituted quinone and a diaminodihydroxybenzene as shown below:



Polymers from various other groups have a ladder type backbone. Most of these polymers have good thermal resistance since they frequently contain aromatic bonds

and more than one bond must be cleaved in order to fragment the macromolecule. However, the reported decomposition temperature may vary from study to study, and it depends on the heating conditions and the choice for the temperature value at which a decomposition is considered as beginning.

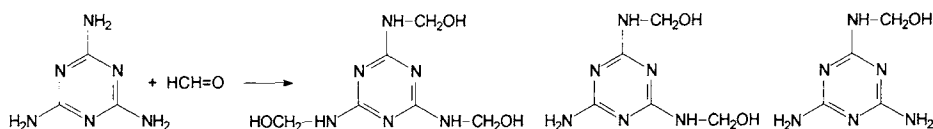
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15.3 THERMOSETTING MELAMINE RESINS

- General aspects

Similar to urea (see Section 13.2), melamine can react with formaldehyde forming a thermosetting resin. Melamine is a trimer of cyanamide and contains three amino groups that offer six possible points of reaction. Since melamine can be considered a triamine of 1,3,5-triazine, this group of resins can be included in the class of polymers with heterocycles in their structure. The first stage of the reaction of melamine with formaldehyde can be written as follows:



Further elimination of water between the methylol groups and amino groups or among themselves generates a thermosetting resin. Similarly to phenol formaldehyde or urea formaldehyde resins, the condensation reaction for melamine is typically carried out in two stages, the resulting material from the first phase having a large number of methylol groups and being still water soluble. In the second stage, the water elimination leads to a crosslinked material. The two-stage process is necessary for handling the resin during the manufacturing of the desired objects.

Both triazine- and urethane-linked networks are highly resistant to paraffin and silicone oils. Triazine-linked networks are resistant to a wide range of organic liquids, whereas urethane-linked networks are attacked by polar organic solvents. Both types are easily attacked by fluorinated species [1].

The Py-GC/MS result for a sample of poly(melamine-co-formaldehyde) methylated, with the molar ratio melamine/formaldehyde/methoxy 1/5.8/5.0, is given in Figure 15.3.1. The polymer has CAS# 68002-20-0 and $M_n = 511$. The pyrolysis was done at 600° C in He at a heating rate of 20° C/ms. The separation was done on a Carbowax column in conditions described in Table 4.2.2. The peak identification for the chromatogram was done using MS spectral library searches only, and it is given in Table 15.3.1.

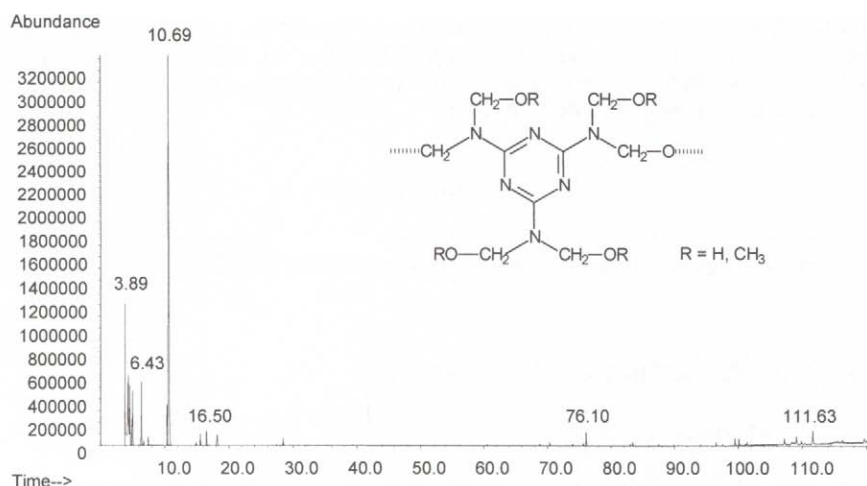


FIGURE 15.3.1. Result for a Py-GC/MS analysis of poly(melamine-co-formaldehyde) methylated, with the molar ratio melamine/formaldehyde/methoxy 1/5.8/5.0, $M_n = 511$. Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 15.3.1. Compounds identified in the pyrogram of poly(melamine-co-formaldehyde) methylated, with the molar ratio melamine/formaldehyde/methoxy 1/5.8/5.0, $M_n = 511$, shown in Figure 15.3.1.

Peak	Compound	Ret. Time	MW	Area %
1	carbon monoxide	4.37	28	9.37
2	carbon dioxide	4.45	44	trace
3	ethane ?	4.62	30	3.54
4	formaldehyde	5.08	30	5.32
5	dimethoxymethane	6.43	76	5.01
6	methylformate	6.77	60	trace
7	isocyanatomethane	7.31	57	trace
8	methanol	10.69	32	71.23
9	2-propenenitrile	14.60	53	trace
10	acetonitrile	15.54	41	trace
11	hydrocyanic acid	16.50	27	1.57
12	water	18.23	18	trace
13	trioxane ?	28.49	90	trace
14	2,3-pyridinediamine	75.67	109	trace
15	4,5-dihydro-2,5-dimethyloxazole	76.10	99	1.62
16	N,N'-diethyl-1,3,5-triazine-2,4,6-triamine	111.63	182	2.34

Results from Table 15.3.1 indicate that among the main decomposition products of these polymers are methanol, CO₂, formaldehyde, and dimethoxymethane. A few nitrogenous compounds also are detected. Some of the decomposition products may be too polar to be detected in the experimental conditions used for the analysis.

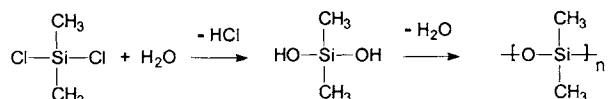
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CHAPTER 16

*Poly(siloxanes) and Other Silicon Containing Polymers***16.1 POLY(SILOXANES)****- General aspects**

Poly(siloxanes) are inorganic-organic polymers that have a backbone formed from alternating oxygen and silicon atoms of the form $[-O-\text{Si}-]_n$. Various substituents are attached to the silicon atom. Poly(dimethyl siloxane), for example, has two methyls attached to the silicon, and this macromolecule can be prepared from the hydrolysis of dimethyldichlorosilane followed by water elimination as shown below:



The starting chlorosilane can be obtained, for example, from the reaction of a silicon copper alloy with methyl chloride. Poly(siloxanes) may have a linear backbone, but also crosslinking of the macromolecular chains is possible through $-\text{O}-$ bridges. This type of polymer may have various degrees of crosslinking, which result in a variety of physical properties, most of them being rubber-like. Low molecular weight poly(siloxanes) are used as silicone fluids and have many practical applications. For low viscosity fluids dimethyldichlorosilane is hydrolyzed and the hydrolysate equilibrated under acid catalysis at 180 °C, with small amounts of hexamethyldisiloxane added as chain terminator.

Silicone rubbers are typically prepared using a polydimethylsiloxane gum obtained by hydrolysis of dimethyldichlorosilane, which is further crosslinked using organic peroxides (typically benzoyl peroxide) at 110–200 °C, under pressure. Cyclic dimethylpolysiloxanes also can be polymerized at 150–200 °C with an alkaline catalyst. Small quantities of hexamethyldisiloxane are added to terminate the siloxane chains. Siloxane rubbers also can be cured by exposure to high energy electrons. Other procedures use curing at room temperature with alkoxysilane as a crosslinking agent and metal salts as catalysts. This type of polymer undergoes curing only when it is exposed to atmospheric moisture and can be used as sealant and also in coatings and adhesives. Special procedures for the preparation of silicones (polydimethylsiloxane) also are reported [1].

Besides methyl groups attached to silicon in the $-\text{Si}-\text{O}-$ chain, another common attached group is phenyl. This group is used together with methyl groups, either as methyl phenyl siloxanes or in copolymers with dimethylsiloxane. Phenyl and methyl substituted cyclic polysiloxanes can be polymerized together using alkaline catalysis and traces of chain terminators to form high viscosity fluids. Other groups (atom) that can

be attached to silicon include hydrogen, octyl, trifluoropropyl, and even phthalocyanin. Poly[oxy(methylsilylene)], CAS# 49718-23-2, can be obtained from methylhydrogen-dichlorosilane by hydrolysis under slightly acidic conditions in the presence of small quantities of trimethylchlorosilane. The material is used as a low viscosity fluid. Poly[oxy(methyloctylsilylene)] is used as a fluid with good lubricating properties. Poly[oxy-(methyl(3,3,3-trifluoropropyl)silylene)] is used as a fluid resistant to chemicals, and poly(oxysiliconphthalocyanin) is used for the preparation of films with special electrical properties.

Several studies regarding pyrolysis and thermal degradation of poly(siloxanes) are reported in literature [2–6], some of these being summarized in Table 16.1.1.

TABLE 16.1.1. Summary of reports on thermal decomposition of poly(siloxanes) [6].

Polymer	Temp. °C	Results	Ref.
poly(oxy-dimethylsilylene) or poly(dimethyl siloxane)	ambient to 500	predominantly cyclic trimer with smaller amounts of cyclic tetramer and higher cyclics; threshold degradation temperature of about 300° C reduced to 100° C by 5% KOH and CH ₄ formed as additional product	7
poly(oxy-dimethylsilylene) or poly(dimethyl siloxane)	470	distribution of cyclic oligomers, n = 3 (243.9 relative mass spec. intensity), n = 4 (100), n = 5 (35.6), n = 6 (37.6), n = 7 (13.1), n = 8 (1.1), n = 9 (0.2)	8
poly(oxy-methyl-3,3,3-trifluoropropyl-silylene)	400	low-molecular weight cyclic oligomers, CF ₂ =CHCH ₃ , CHF ₃	9
poly(oxy-methyl-3,3,3-trifluoropropyl-silylene)	615 for 30 s	cyclic methyl-(3,3,3-trifluoropropyl)siloxanes, CH ₄ , CHF ₃ , CF ₂ =CHCH ₃ , CH ₂ =CHCF ₃	10
poly(oxy-methylphenyl-1,4-silphenylene-silylene)	ambient to 500	benzene, diphenylmethylsilane, triphenylmethylsilane, and higher linear oligomers	11
poly(oxy-methylphenyl-silylene)	ambient to 500	mixture of all possible stereoisomeric cyclic trimers and tetramers with small amounts of pentamer, benzene, and two more complex oligomers	12
poly(oxy-phenyl--butoxysilylene)	430–500	CO, H ₂ and hydrocarbons	13
poly(oxy-tetramethyl-1,3-silphenylene-silylene-hexafluoropropylene-phenylene)	615 for 30 s	HF (15–18%), methane, methyltrifluorosilane, dimethyldifluorosilane, benzene, toluene, phenyldifluoromethane	10
poly(oxy-tetramethyl-1,3-silphenylene-silylene-tetrafluoroethylene-phenylene)	615 for 30 s	HF (15–18%), methane, methyltrifluorosilane, dimethyldifluorosilane, benzene, toluene, phenyldifluoromethane	10
poly(oxy-tetramethyl-1,4-silphenylene-silylene)	500 in argon	methane, HSi(CH ₃) ₂ -O-Si(CH ₃) ₂ H, benzene, cyclic trimer of dimethylsiloxane, and various higher chain fragments	14
poly(oxy-tetramethyl-1,4-silphenylene-silylene)	ambient to 500	cyclic trimer and tetramer of dimethylsiloxane and a complex mixture of higher linear and cyclic oligomers	15

The results for a Py-GC/MS analysis of a sample of poly(dimethylsiloxane) or poly(oxy-dimethylsilylene) with $M_w = 95,000$ are shown in Figure 16.1.1. The polymer has the CAS# 9016-00-6 and the idealized formula $[-Si(CH_3)_2O-]_n$. The pyrolysis was done at 600° C in He at a heating rate of 20° C/ms. The separation was done on a Carbowax column (60 m, 0.32 mm i.d., 0.32 μ m film thickness) with the GC starting at 40° C with a ramp of 2° C/min. up to 240° C and a final oven time of 20 min. (see Table 4.2.2). The MS was operated in EI+ mode. The peak identification for the chromatogram was done using MS spectral library searches only, and it is given in Table 16.1.2.

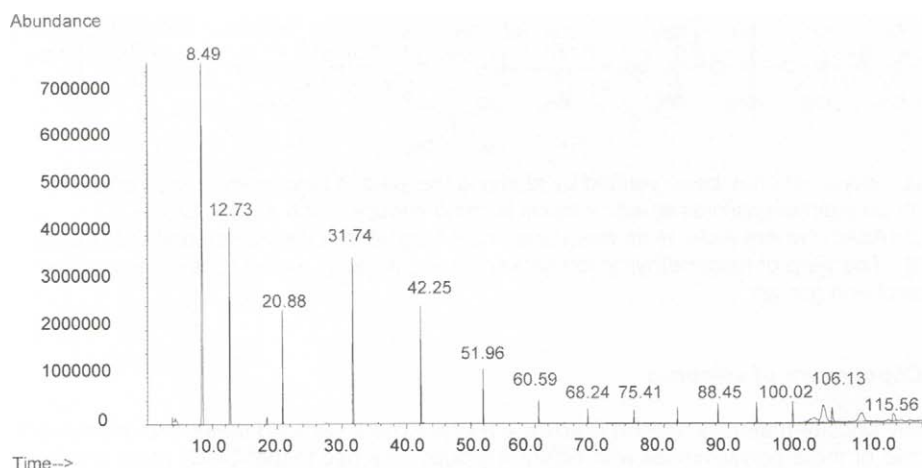
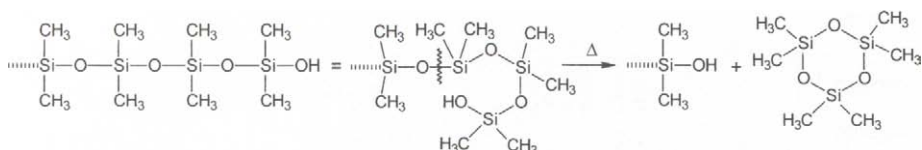


FIGURE 16.1.1. Result for a Py-GC/MS analysis of poly(dimethylsiloxane) $M_w = 95,000$. Pyrolysis done on 0.4 mg material at 600°C in He, with the separation on a Carbowax type column.

TABLE 16.1.2. Compounds identified in the pyrogram of poly(dimethylsiloxane) $M_w = 95,000$ shown in Figure 16.1.1.

Peak	No. Si	Compound	Ret. time	MW	Area %
1	Si ₃	hexamethylcyclotrisiloxane	8.49	222	40.07
2	Si ₄	octamethylcyclotetrasiloxane	12.73	296	15.64
3		water	18.46	18	0.67
4	Si ₅	decamethylcyclopentasiloxane	20.88	370	6.03
5	Si ₆	dodecamethylcyclohexasiloxane	31.74	444	9.58
6	Si ₇	tetradecamethylcycloheptasiloxane	42.25	518	6.68
7	Si ₈	hexadecamethylcyclooctasiloxane	51.96	592	2.61
8	Si ₉	octadecamethylcyclononasiloxane	60.59	666	1.06
9	Si ₁₀		68.24	740	0.72
10	Si ₁₁		75.41	814	0.70
11	Si ₁₂		82.15	888	0.87
12	Si ₁₃		88.45	962	1.13
13	Si ₁₄		94.12	1036	0.31
14	Si ₁₅		94.40	1110	1.59
15	Si ₁₆		100.02	1184	7.89
16	Si ₁₇		106.13	1258	2.44
17	Si ₁₈		115.56	1332	1.98

The pyrolysate of poly(dimethyl siloxane) consists of various cyclic siloxanes such as hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, etc. The formation of these compounds is exemplified below for the formation of a hexamethylcyclotrisiloxane:



The mechanism has been verified by studying the yield of hexamethylcyclotrisiloxane from poly(dimethylsiloxane) with various terminal groups, such as OH, OCH₃, OCu(AcAc) (where AcAc is an acetylacetonate fragment), OFe(AcAc), and OZr(AcAc) [16]. The yield of hexamethylcyclotrisiloxane is significantly higher for the case of free silanol end groups.

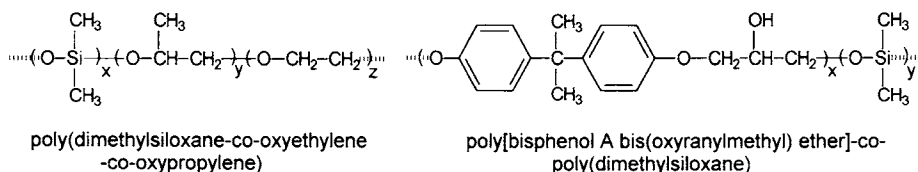
- Copolymers of silicones

Many silicone materials used in practice are copolymers. Among these, the copolymers of two or more polysiloxanes with different groups attached to the -Si-O- chain are the most common. These copolymers are typically obtained from dichloroalkyl or aryl silanes, which are polymerized either with an acidic or alkaline catalyst. Further crosslinking can be done using organic peroxides and end chain terminators to eliminate the possible free silanol end groups. A common copolymer is obtained following this procedure from dichlorodimethylsilane, dichloromethylphenylsilane, and hexamethylcyclotrisiloxane at 150–200° using an alkaline catalyst and traces of hexamethyldisiloxane. Organic peroxides can be used similarly to the case of homopolymers for curing and to generate an elastomer with good mechanical properties. Thermal properties of some of these copolymers reported in literature are summarized in Table 16.1.3 [6].

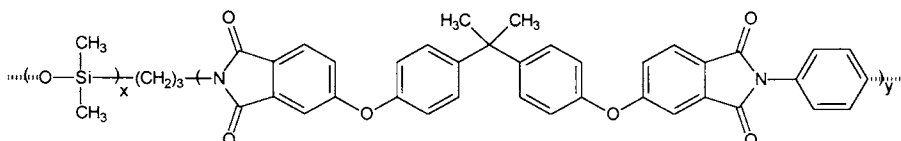
TABLE 16.1.3. Summary regarding reports on thermal decomposition of poly(siloxanes) [6].

Polymer	Temp. °C	Results	Ref.
poly(dimethyl siloxane-co-diphenyl siloxane)	ambient to 500	complex mixture of cyclic oligomers, which have been individually identified, whose composition varies with the dimethyl/diphenyl ratio; small amounts of benzene	17
poly(dimethyl siloxane-co-phenylmethyl siloxane)	ambient to 500	complex mixture of cyclic oligomers, which have been individually identified, whose composition varies with the dimethyl/methylphenyl ratio; small amounts of benzene	18
poly(oxy-tetramethyl-1,3-silphenylene-siloxane-co-dimethylsiloxane)	ambient to 500	cyclic trimer and tetramer of dimethylsiloxane and a complex mixture of higher linear and cyclic oligomers	15
poly(boron tri(dimethylsiloxane) nonlinear)	250–350	molecular weight increases; traces of cyclic products [(CH ₃) ₂ SiO] ₃ and [(CH ₃) ₂ SiO] ₄	19
poly(ethenylmethyl siloxane-co-3,3,3-trifluoropropylmethyl siloxane)	500	complex mixture of cyclic oligomers	20
poly(dimethyl siloxane-co-cyanopropylmethyl siloxane)	500	complex mixture of cyclic oligomers	20

Other copolymers have additional groups included in the backbone. Ether groups are common in such copolymers, and the idealized structures of two such compounds are shown below:

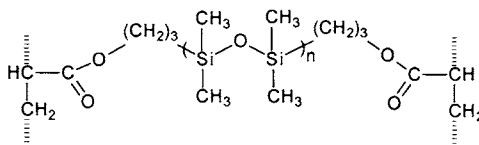


Poly(dimethylsiloxane-co-oxyethylene-co-oxypropylene) is used as a surfactant, dispersant, and wetting agent, while poly[bisphenol A bis(oxyranilylmethyl) ether]-co-poly(dimethylsiloxane) is used as an epoxy resin. More complicated silicone copolymers also were synthesized such as the silicone polyetherimide shown below:



This copolymer can be obtained from a polydimethylsiloxane that has aminoalkyl end groups in a reaction with the polyetherimide formed from the reaction of a bis(ether anhydride) with diaminobenzene. The material is fire resistant and is used in cable insulations. Among other more complex copolymers with practical applications are poly[2,2-propanebis(4-phenyl)-carbonate]-*block*-poly(dimethylsiloxane)] and a silicone phenol formaldehyde copolymer obtained in two steps, the first being the heating of a polydimethylsiloxane that has reactive end groups with glycerol, and the second step being the reaction with a phenol formaldehyde resin.

A different way to introduce silicone type sequences in copolymers is to attach acrylate end groups to a poly[oxy(dimethylsilylene)], followed by copolymerization in a vinyl type polymer. The introduction of silicone groups leads to a crosslinked material similar to that obtained with poly(ethylene glycol) dimethacrylate. The structure of a copolymer with silicone crosslinking bridges is shown below:



Thermal decomposition of poly(alkylsiloxane) copolymers is similar to that of poly(dimethylsiloxane), the main compound generated from the siloxane moiety being cyclic siloxanes. The results for a Py-GC/MS analysis of a sample of poly(dimethylsiloxane-co-methylphenylsiloxane) with phenyl/methyl mole ratio 1/1 are shown in Figure 16.1.2. The polymer idealized formula is $[-\text{Si}(\text{CH}_3)_2\text{O}-]_x [-\text{Si}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{O}-]_y$ where $x = y$. The pyrolysis was done at 600°C in He with the analysis done in the same conditions as for other examples previously discussed (see Table 4.2.2). The peak identification for the chromatogram was done using MS spectral library searches only and it is given in Table 16.1.4.

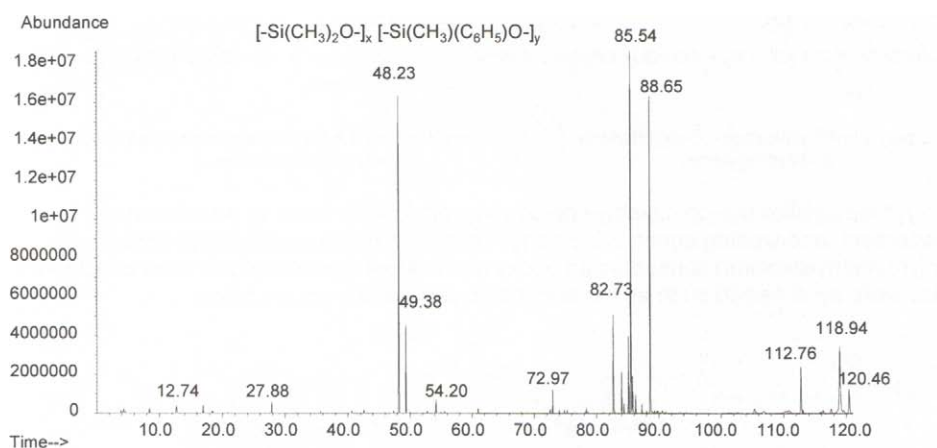


FIGURE 16.1.2. Result for a Py-GC/MS analysis of poly(dimethyl-siloxane-co-methylphenylsiloxane). Pyrolysis done on 0.4 mg material at 600° C in He, with the separation on a Carbowax type column.

TABLE 16.1.4. Compounds identified in the pyrogram of poly(dimethyl-siloxane-co-methylphenylsiloxane) shown in Figure 16.1.2.

Peak	Compound	Ret. time	MW	Area %
1	2,2,4,4,6,6-hexamethyl-1,3,5,2,4,6-trioxatrisilane (hexamethylcyclotrisiloxane)	8.44	222	2.15
2	octamethylcyclotetrasiloxane	12.75	296	0.94
3	benzene	12.81		trace
4	trimethyl silanol	16.98	90	0.45
5	decamethylcyclopentasiloxane	20.88	370	trace
6	1-methoxy-1-methyl-1-(1-methyl-1-silaethoxy)-1-silaethane	27.88	164	0.44
7	dodecamethylcyclohexasiloxane	31.74	444	trace
8	2-methoxy-2,4,4,6,6-pentamethyl-1,3,5,2,4,6-trioxatrisilane	35.70	238	0.34
9	tetradecamethylcycloheptasiloxane	42.25	518	trace
10	2-methoxy-2,4,4,6,6,8,8-heptamethyl-1,3,5,7,2,4,6,8-tetraoxatetrasiloxane	42.64	312	trace
11	pentamethylphenylcyclotrisiloxane	48.24	284	16.76
12	heptamethylphenylcyclotetrasiloxane	49.38	358	4.08
13	nonamethylphenylcyclopentasiloxane	54.20	432	0.52
14	undecamethylphenylcyclohexasiloxane	60.98	506	0.23
15	tridecamethylphenylcycloheptasiloxane	67.89	580	trace
16	2-phenoxy-2,4,4,6,6-pentamethyl-1,3,5,2,4,6-trioxatrisilane	72.57	300	0.63
17	1-methoxy-1-methyl-1-(1-phenyl-1-silaethoxy)-1-silaethane	72.97	226	1.06
18	2-phenoxy-2,4,4,6,6,8,8-heptamethyl-1,3,5,7,2,4,6,8-tetraoxatetrasiloxane ?	74.04	374	0.16
19	2-methoxy-2,4,4,6,6,8,8-hexamethyl-6-phenyl-1,3,5,7,2,4,6,8-tetraoxatetrasiloxane ?	74.84	374	0.16
20	2-methoxy-4-phenoxy-2,4,6,6-tetramethyl-1,3,5,2,4,6-trioxatrisilane	75.30	316	0.61
21	unknown [281(100), 135(33), 197(15), 343(12), ...419(2)]	78.36		0.25
22	isomer of 2,2,4,4,6,8-hexamethyl-6,8-diphenyl-1,3,5,7,2,4,6,8-tetraoxatetrasiloxane	82.73	420	4.64

TABLE 16.1.4 (continued). Compounds identified in the pyrogram of poly(dimethylsiloxane-co-methylphenylsiloxane) shown in Figure 16.1.2.

Peak	Compound	Ret. time	MW	Area %
23	isomer of 2,2,4,4,6,8-hexamethyl-6,8-diphenyl-1,3,5,7,2,4,6,8-tetraoxatetrasiloxane	84.04	420	2.11
24	2,2,4,4,6,6,8,10-octamethyl-8,10-diphenyl-1,3,5,7,9,2,4,6,8,10-pentaoxapentasildecane	84.42	494	0.45
25	isomer of 2,2,4,4,6,8-hexamethyl-6,8-diphenyl-1,3,5,7,2,4,6,8-tetraoxatetrasiloxane	85.14	420	3.73
26	2,2,4,6-tetramethyl-4,6-diphenyl-1,3,5,2,4,6-trioxatrisilane	85.55	346	19.41
27	isomer of 2,2,4,4,6,8-hexamethyl-6,8-diphenyl-1,3,5,7,2,4,6,8-tetraoxatetrasiloxane	85.79	420	2.07
28	2,2,4,4,6,6,8,10-octamethyl-8,10-diphenyl-1,3,5,7,9,2,4,6,8,10-pentaoxapentasildecane	86.28	494	0.89
29	isomer of 2,2,4,4,6,6,8,10-octamethyl-8,10-diphenyl-1,3,5,7,9,2,4,6,8,10-pentaoxapentasildecane	87.28	494	0.41
30	2,2,6,6-tetramethyl-4,4-diphenyl-1,3,5,2,4,6-trioxatrisilane	88.66	346	16.80
31	unknown[269(100), 253(57), 343(38), 127(23), ...405(3)]	105.32		0.40
32	2,4,6,6,8-hexamethyl-1,4,8-triphenyl-1,3,5,7,2,4,6,8-tetraoxatetrasiloxane	112.76	482	3.85
33	isomer of 2,4,6,6,8-hexamethyl-1,4,8-triphenyl-1,3,5,7,2,4,6,8-tetraoxatetrasiloxane	118.94	482	13.70
34	isomer of 2,4,6,6,8-hexamethyl-1,4,8-triphenyl-1,3,5,7,2,4,6,8-tetraoxatetrasiloxane	120.45	482	2.75

Some of the identifications given in Table 16.1.4 are only tentative because the corresponding spectra are not available in common mass spectral libraries (NIST, Wiley). For example, the spectrum of undecamethylphenylcyclohexasiloxane is not available, and the spectrum for nonamethylphenylcyclotrisiloxane given only in Wiley 4 mass spectral library does not show ions with $m/z > 400$ a.u. The spectra of two compounds available in Wiley 6, namely pentamethylphenylcyclotrisiloxane and heptamethylphenylcyclotetrasiloxane are shown in Figure 16.1.3a, and those of undecamethylphenylcyclohexasiloxane and nonamethylphenylcyclotrisiloxane are shown in Figure 16.1.3b.

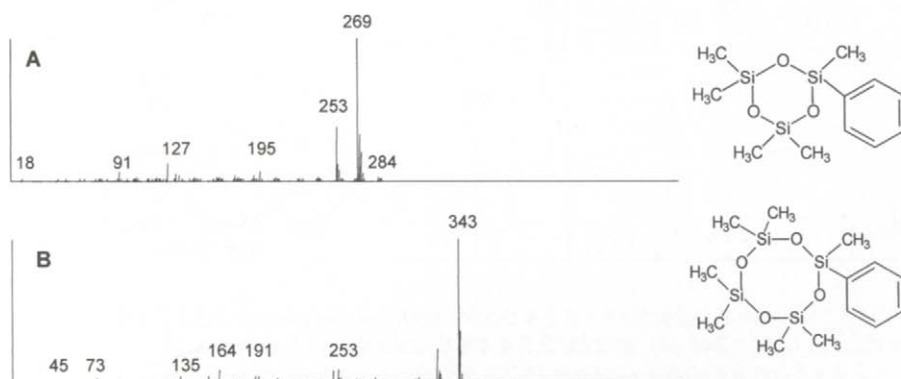


FIGURE 16.1.3a. Mass spectra for pentamethylphenylcyclotrisiloxane MW = 284 (A), and heptamethylphenylcyclotetrasiloxane MW = 358 (B) from mass spectral libraries.

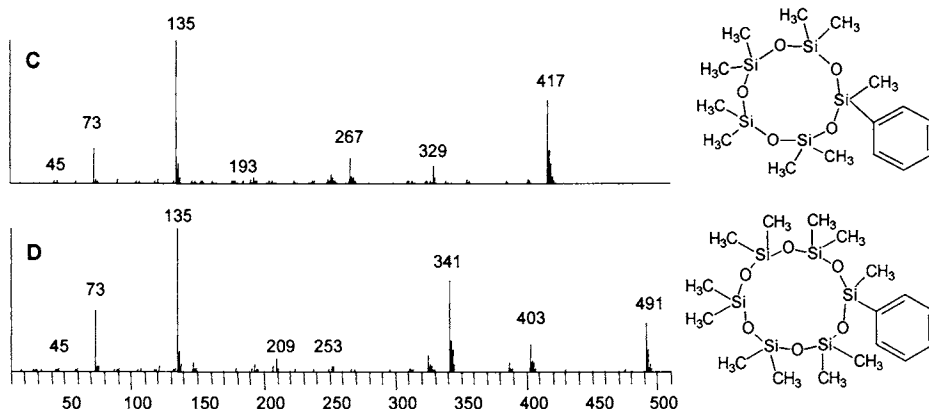


FIGURE 16.1.3b. Tentative mass spectra for nonamethylphenylcyclopentasiloxane MW = 432 (C) and for undecamethylphenylcyclohexasiloxane MW = 506 (D) not found in common mass spectral libraries.

A similar situation is encountered for cyclosiloxanes with two phenyl substituents. Only the spectrum for 2,2,4,6-tetramethyl-4,6-diphenyl-1,3,5,2,4,6-trioxatrisilane MW = 346 is available in common mass spectral libraries. The spectrum for this compound and that for 2,2,4,4,6,8-hexamethyl-6,8-diphenyl-1,3,5,7,2,4,6,8-tetraoxatetrasiloxane MW = 420 (or a position isomer) are given in Figures 16.1.4a, and the spectrum for 2,2,4,4,6,6,8,10-octamethyl-8,10-diphenyl-1,3,5,7,9,2,4,6,8,10-pentaoxapentasildecane MW = 494 (or a position isomer) is given in Figures 16.1.4b.

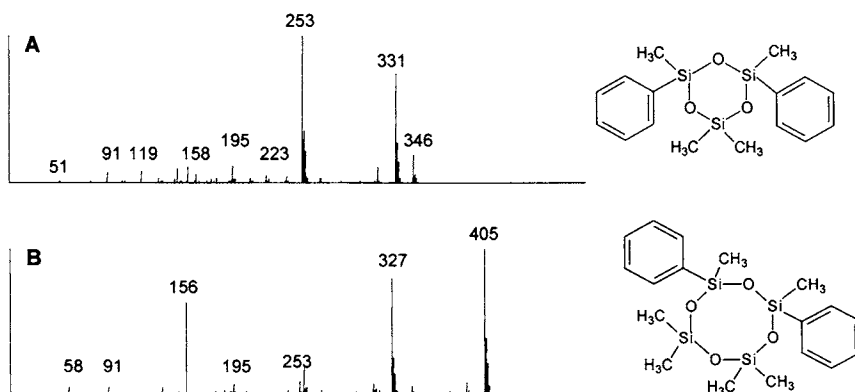
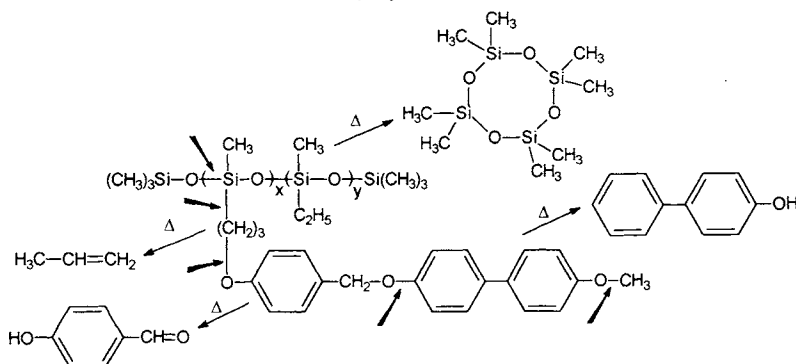


FIGURE 16.1.4a. Mass spectra for 2,2,4,6-tetramethyl-4,6-diphenyl-1,3,5,2,4,6-trioxatrisilane MW = 346 (A), and for 2,2,4,4,6,8-hexamethyl-6,8-diphenyl-1,3,5,7,2,4,6,8-tetraoxatetrasiloxane MW = 420 (or a position isomer) (B)

silicone backbone were the characteristic polycyclosiloxanes, such as decamethylcyclopentasiloxane and dodecamethylcyclohexasiloxane. The side groups generated characteristic fragments depending on the R^a and/or R^b substituent. For example, for R^a being 4-(4-methoxyphenyl)-1-(phenylmethoxy)phenyl, and R^b being ethyl, the compounds detected in the pyrolysate were propene, methylbenzene, benzaldehyde, phenol, chromane, 4-methylbenzaldehyde, 4-methoxyphenyl-1-methanol, biphenyl, 4-phenylphenol, and 1-methoxy-4-(4-methoxyphenyl)benzene. The result suggested that the pyrolysis occurs by random scission of various bonds, as indicated in the scheme shown below for one of the polymers:



As expected, the C-O and Si-O bonds were easier to break compared to other bonds. The study proved the possibility to analyze these polymers using pyrolysis and also investigated their thermal stability.

References 16.1

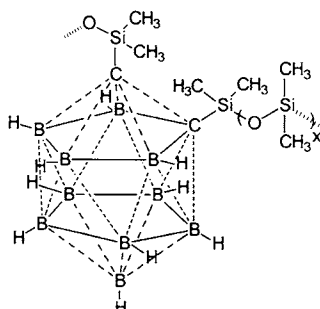
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16.2 OTHER SILICON CONTAINING POLYMERS

- General aspects

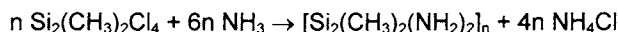
A material with interesting mechanical properties is obtained from a fluid polydimethylsiloxane by heating it at 150–250 °C with boric oxide and ferric chloride for several hours. The resulting material (Silly putty) behaves as a very viscous fluid on storage but shows elastic rebound on sudden impact. During the heating, boron atoms are incorporated into the linear structure of polydimethylsiloxane, leading to crosslinking, which changes the material properties. Organically modified borosilicate materials have practical utility and occasionally are analyzed using pyrolytic techniques [1]. Another types of boron containing polymers are polycarborane siloxanes. The idealized structure of polycarborane dimethylsiloxane is shown below:



The polysiloxane sequence can be shorter or longer, the compounds with about 20% carborane being typically used. Polycarborane siloxanes have high resistance to heating and are used for various purposes, including stationary phases for gas chromatography [2] and in medical applications.

Besides poly(siloxanes), a few other silicone containing polymers have been synthesized. One such polymer is poly(dimethy-1,4-silphenylene). Thermal decomposition of this polymer at 400° C in argon [3] generates methane, dimethylsilane, benzene, dimethylphenylsilane, $\text{HSi}(\text{CH}_3)_2\text{-C}_6\text{H}_4\text{-SiH}(\text{CH}_3)_2$, $\text{H}(\text{Si}(\text{CH}_3)_2\text{-C}_6\text{H}_4)_2\text{-H}$, dimethyl-diphenylsilane, and $\text{C}_6\text{H}_4\text{-(Si}(\text{CH}_3)_2\text{-C}_6\text{H}_4)_2\text{H}$.

Another special type of silicone containing polymers is polysilazanes. These materials are used in for the preparation of high performance ceramics, silicon nitride, etc. Polysilazane can be prepared from substituted methylchlorosilanes and gaseous ammonia in the following reaction [4]:



Pyrolysis of the formed polysilazane at 750° C generates several alkylsilanes such as dimethylsilane, trimethylsilane, ethyldimethylsilane, tetramethyldisiloxane, pentamethyldisiloxane, methylenebisdimethylsilane, hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, etc. The presence of the cyclic compounds similar to those from poly(dimethylsiloxane) was an indication that some polysiloxane sequences may be present in the polymer. Thermal degradation studied between 350° C and 650° C showed the formation of some hydrogen, methane, ethane, and propene.

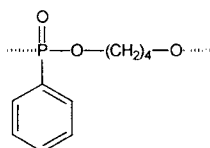
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CHAPTER 17

*Polymers Containing Phosphorus in the Backbone***17.1 POLYMERS CONTAINING PHOSPHORUS AND OXYGEN IN THE BACKBONE****- General aspects**

Only very few polymers contain besides carbon and hydrogen only phosphorous and oxygen in their backbone. One example is poly(oxytetramethylene oxyphenyl phosphono) with the structure indicated below:



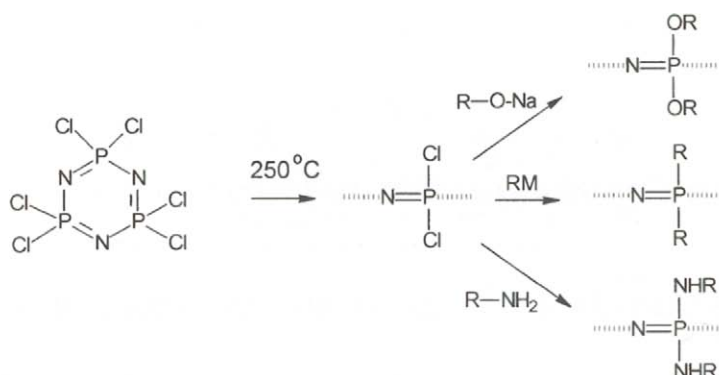
The thermal stability of this polymer has been studied, and by heating from ambient to 500° C the polymer generates butadiene, tetrahydrofuran, dihydrofuran, water, the cyclic ester of phenylphosphonic acid and 1,4-butanediol, phenylphosphonic acid, and butanediol [1]. The same report evaluates thermal decomposition of this polymer end capped with phenylisocyanate. In addition to the same compounds as for the main polymer, CO₂ and aniline were detected from the polymer decomposition.

References 17.1

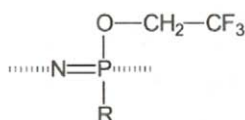
1. N. Grassie, D. H. MacKerron, *Polym. Degrad. Stab.*, 5 (1983) 43.

17.2 POLYMERS CONTAINING PHOSPHORUS AND NITROGEN IN THE BACKBONE**- General aspects**

The best known polymers from this group are the polyphosphazenes. Several phosphazene type polymers have practical applications as non-burning foam insulation materials. Other applications also are known especially for copolymers with polyurethanes, the polyphosphazenes bringing flame retardant properties. Also, as biodegradable materials these polymers can be used for control release materials for drug delivery. Polyphosphazenes can be obtained from heating hexachlorocyclotriphosphazene (NPCl₂)₃ for a period of time (a day or more) with specific reagents, as shown in the following scheme [1]:



Polymers with different groups attached to the phosphorus atom can be obtained from phosphazene cyclic trimers or tetramers with mixed halogen and alkyl or aryl side groups by a similar procedure. Further attachment of side groups, such as fluoroalkoxy, can be achieved by treatment of the polymer with excess of sodium fluoroalkoxides [2]. By this procedure are obtained, for example, poly(fluoroalkoxyphosphazenes) with the structure shown below:



$R = \text{O}-\text{CH}_2\text{CH}_3, \text{C}(\text{CH}_3)_3, \text{C}_6\text{H}_5, \text{CH}_3, \text{C}_2\text{H}_5, \text{etc.}$

In general, polyphosphazenes are not very resilient to heating, but their thermal decomposition occurs with a high degree of crosslinking and the formation of a dense structure that acts as a flame retardant [3]. For some copolymers, the presence of phosphazene sequences enhances the thermal stability. Some other literature reports regarding thermal decomposition of these compounds are given in Table 17.2.1.

TABLE 17.2.1. Summary regarding reports on thermal decomposition of poly(phosphazenes) [4].

Polymer	Temp. °C	Results	Ref.
poly(bis(trifluoroethoxy)-phosphazene)	150-400	cyclic trimer, tetramer, pentamer, hexamer, and higher oligomers, 1,1,1-trifluoro-2-chloroethane (due to residual chlorine in the polymer)	5
poly(diphenoxy-phosphazene)	100-400	cyclic tetramer, trimer and higher oligomers, chlorobenzene (due to residual chlorine in the polymer), phenol, triphenylphosphate	6
poly(diphenoxy-phosphazene) residual Cl < 0.05%	ambient to 480	traces of phenol, phenoxy cyclic trimer and monochlorophenoxy cyclic trimer	7
poly(diphenoxy-phosphazene) residual Cl < 2.4%	ambient to 480	phenoxy cyclic trimer and tetramer, monochloropentaphenoxy cyclic trimer, monochloroheptaphenoxy cyclic tetramer, dichlorohexaphenoxy cyclic tetramers	7

TABLE 17.2.1 (continued). *Summary regarding reports on thermal decomposition of poly(phosphazenes) [4].*

Polymer	Temp. °C	Results	Ref.
poly(diphenoxy-phosphazene) residual Cl < 9.9%	ambient to 480	Phenoxy cyclic trimer and tetramer, monochloropentaphenoxy cyclic trimer, monochloroheptaphenoxy cyclic tetramer, dichlorohexaphenoxy cyclic tetramers, dichlorotetraphenoxy cyclic trimers, trichloropentaphenoxy cyclic tetramers, HCl	7
poly[bis(p-R-phenoxy)-phosphazenes]	700	50% char	8

Besides the phosphazenes other polymers containing nitrogen and phosphorus are known [9]. Some of such polymers are used as flame retardant additives to other polymers (see Section 5.4).

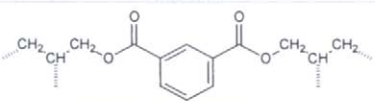
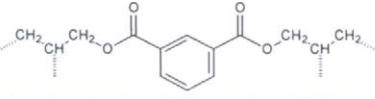
References 17.2

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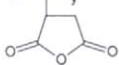
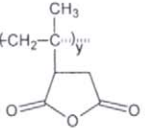
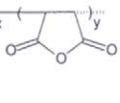

List of Thermograms of Various Polymers

Figure	Polymer
2.1.1	poly(ethylene-alt-chloro-trifluoroethylene)
2.2.3	polyethylene
3.1.2	poly(diallyl isophthalate)
6.2.1	polystyrene
6.3.1	poly(vinyl chloride)
6.3.6	polytetrafluoroethylene
6.3.11	poly(vinylidene fluoride-co-hexafluoro-propylene)
6.5.1	poly(vinyl alcohol)
6.7.1	poly(acrylic acid)
10.1.10	poly(ethylene terephthalate)
12.1.1	poly(1,4-phenylene sulfide)
13.3.1	polycaprolactam or nylon 6
13.3.7	poly(phenylene isophthalamide) or Nomex
13.4.2	poly[4,4'-hexafluoro-isopropylidene)-diphthalic anhydride-alt-acridine yellow G] HCl
15.1.1	poly(thiophene-2,5-diyl)
15.1.3	poly(3-hexylthiophene-2,5-diyl)

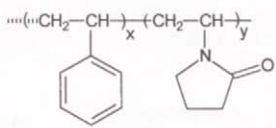
List of Pyrograms of Various Polymers

Figure	Polymer name	CAS#	M _w	Structure
3.1.3	poly(diallyl isophthalate)	25035-78-3	500,000	
3.1.4	poly(diallyl isophthalate) at 850° C	25035-78-3	500,000	
3.1.7	poly(vinyl ethyl ether) 0.4 mg	25104-37-4	3,800	$[-CH_2CH(OCH_2CH_3)-]_n$
3.1.8	poly(vinyl ethyl ether) 0.8 mg	25104-37-4	3,800	$[-CH_2CH(OCH_2CH_3)-]_n$
4.1.1	poly(vinyl ethyl ether) (window)	25104-37-4	3,800	$[-CH_2CH(OC_2H_5)-]_n$
4.1.2	poly(vinyl ethyl ether) (window)	25104-37-4	3,800	$[-CH_2CH(OC_2H_5)-]_n$
4.1.6	poly(acrylonitrile-co-methyl acrylate) (duplicates)	24968-79-4		$[-CH_2-CH(CN)-]_x[-CH_2-CH(COOCH_3)-]_y$
4.3.1	polypropylene isotactic and syndiotactic	9003-07-0	12,000 and 127,000	$[-CH_2CH(CH_3)-]_n$
4.3.2	polypropylene (amorphous) (window)	9003-07-0	14,000	$[-CH_2CH(CH_3)-]_n$
6.1.2	polyethylene	9002-88-4		$(-CH_2CH_2-)_n$
6.1.4	polyethylene (window)	9002-88-4		$(-CH_2CH_2-)_n$
6.1.4	polyethylene high density and low density (window)	9002-88-4		$(-CH_2CH_2-)_n$
6.1.6	polyethylene medium density	9002-88-4		$(-CH_2CH_2-)_n$
6.1.7	impure polyethylene medium density ion 59	9002-88-4		$(-CH_2CH_2-)_n$
6.1.8	poly(ethylene-co-acrylic acid) 15 wt % acrylic acid	9010-77-9		$(-CH_2CH_2-)_x[-CH_2CH(COOH)-]_y$
6.1.9	poly(ethylene-co-acrylic acid) 15 wt % acrylic acid (window)	9010-77-9		$(-CH_2CH_2-)_x[-CH_2CH(COOH)-]_y$
6.1.10	poly(ethylene-co-methacrylic acid) (10% wt. methacrylic acid)	25053-53-6		$(-CH_2CH_2)_x[-CH_2C(CH_3)(COOH)-]_y$
6.1.11	poly(ethylene-co-methyl acrylate) (21.5% wt. methyl acrylate) (butylated hydroxyethylbenzene inhibitor)	25103-74-6	79,000 M _n 15,000	$(-CH_2CH_2)_x[-CH_2CH(COOCH_3)-]_y$
6.1.12	poly(ethylene-co-methyl acrylate) (6.5% wt. methyl acrylate) (butylated hydroxyethylbenzene inhibitor)	25103-74-6		$(-CH_2CH_2)_x[-CH_2CH(COOCH_3)-]_y$
6.1.13	poly(ethylene-co-vinyl acetate) (BHT inhibitor)	24937-78-8		$(-CH_2CH_2-)_x[-CH_2CH(OOCCH_3)-]_y$

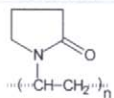

List of Pyrograms of Various Polymers (continued)

Figure	Polymer name	CAS#	M _w	Structure
6.1.14	poly(ethylene- <i>graft</i> -maleic anhydride) (3% wt. maleic anhydride)	106343-08-2		$\text{---}(\text{CH}_2\text{---CH}_2)_x\text{---}(\text{CH}_2\text{---CH})_y\text{---}$ 
6.1.16 A	polypropylene (isotactic)	9003-07-0	12,000	$[\text{---CH}_2\text{CH}(\text{CH}_3)\text{---}]_n$
6.1.16 B	polypropylene (syndiotactic)	9003-07-0	127,000	$[\text{---CH}_2\text{CH}(\text{CH}_3)\text{---}]_n$
6.1.17	polypropylene isotactic and syndiotactic (window)	9003-07-0	12,000	$[\text{---CH}_2\text{CH}(\text{CH}_3)\text{---}]_n$
6.1.21	polypropylene (amorphous)	9003-07-0	14,000	$[\text{---CH}_2\text{CH}(\text{CH}_3)\text{---}]_n$
6.1.22	poly(propylene-co-1-butene) 14 wt % butene	29160-13-2		$[\text{---CH}_2\text{CH}(\text{CH}_3)\text{---}]_x [\text{---CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{---}]_y$
6.1.23	poly(propylene-co-1-butene) 14 wt % butene (window)	29160-13-2		$[\text{---CH}_2\text{CH}(\text{CH}_3)\text{---}]_x [\text{---CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{---}]_y$
6.1.24	polypropylene- <i>graft</i> -maleic anhydride or polypropylene- <i>graft</i> -poly[3-(1-methyl-1-propenyl)-3,4-dihydrofuran-2,5-dione]	107001-49-0	9,100	$\text{---}(\text{CH}_2\text{---CH})_x\text{---}(\text{CH}_2\text{---C})_y\text{---}$ 
6.1.25	polyisobutylene	9003-27-4	420,000	$[\text{---CH}_2\text{C}(\text{CH}_3)_2\text{---}]_n$
6.1.27	poly(4-methyl-1-pentene) (isotactic)	25068-26-2	high	$(\text{---CH}_2\text{CH}[\text{CH}_2\text{CH}(\text{CH}_3)_2]\text{---})_n$
6.1.29	poly(propylene- <i>alt</i> -ethylene) multi arm or hydrogenated polyisoprene 0.2% antioxidant	127883-08-3		$[\text{---CH}_2\text{CH}_2\text{---CH}(\text{CH}_3)\text{CH}_2\text{---}]_n$
6.1.30	poly(propylene- <i>alt</i> -ethylene) multi arm or hydrogenated polyisoprene 0.2% antioxidant (window)	127883-08-3		$[\text{---CH}_2\text{CH}_2\text{---CH}(\text{CH}_3)\text{CH}_2\text{---}]_n$
6.2.2	polystyrene	9003-53-6	280,000	$[\text{---CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{---}]_n$
6.2.4	poly(styrene-co-divinylbenzene) 2% crosslinked	69011-14-9		$[\text{---CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{---}]_x [\text{---CH}_2\text{CH}(\text{C}_6\text{H}_4\text{---CHCH}_2\text{---})\text{---}]_y$
6.2.5	poly(styrene-co-acrylonitrile) 25 wt % acrylonitrile	9003-54-7	165,000	$[\text{---CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{---}]_x [\text{---CH}_2\text{CH}(\text{CN})\text{---}]_y$
6.2.6	poly(styrene-co-methyl methacrylate) 40% styrene	25034-86-0	100,000-150,000	$[\text{---CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{---}]_x [\text{---CH}_2\text{C}(\text{CH}_3)(\text{COOCH}_3)\text{---}]_y$
6.2.8	poly(styrene-co-maleic anhydride) 7 wt % maleic anhydride	9011-13-6	224,000	$\text{---}(\text{CH}_2\text{---CH})_x\text{---}(\text{CH}_2\text{---C})_y\text{---}$ 
6.2.10	polystyrene- <i>block</i> -polybutadiene 30 wt % styrene, 80% diblock (added antioxidant)	9003-55-8		$\text{---}(\text{CH}_2\text{---CH})_x\text{---}(\text{CH}_2\text{---CH=CH---CH}_2\text{---})_y\text{---}$ 
6.2.11	poly(2-vinylpyridine-co-styrene) styrene 30%	24980-54-9	220,000	$[\text{---CH}_2\text{CH}(\text{2-C}_5\text{H}_4\text{N})\text{---}]_x [\text{---CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{---}]_y$

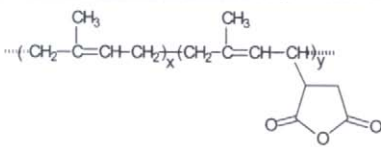
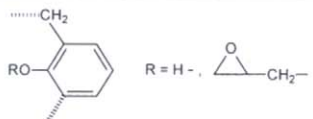
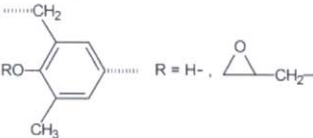
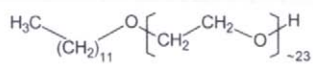
List of Pyrograms of Various Polymers (continued)

Figure	Polymer name	CAS#	M _w	Structure
6.2.14	poly(1-vinylpyrrolidone-co-styrene)	25086-29-7		
6.2.15	polystyrene with poly(ethylene glycol)(16) crosslinked 4-benzyloxybenzyl alcohol 0.8-1.5 mmol/g (Wang resin)			see page 264
6.2.16	polystyrene with poly(ethylene glycol)(16) crosslinked 4-benzyloxybenzyl alcohol 0.8-1.5 mmol/g (Wang resin) (window)			see page 264
6.2.17	poly(vinyltoluene)	9017-21-4	80,000	$[-CH_2CH(C_6H_4CH_3)-]_n$
6.2.18	poly(4-ethylstyrene-co-divinylbenzene)	9043-77-0		
6.2.19	poly(α -methylstyrene)	25014-31-7	M _n 790	$[-CH_2C(CH_3)(C_6H_5)-]_n$
6.3.2	poly(vinyl chloride)	9002-86-2	85,000	$[-CH_2CH(Cl)-]_n$
6.3.3	poly(vinyl chloride-co-vinyl acetate) 86 wt % vinyl chloride	9003-22-9	M _n 27,000	$[-CH_2CH(Cl)-]_x [-CH_2CH(OCOCH_3)-]_y$
6.3.4	poly(vinyl chloride-co-acrylonitrile) 20 wt % acrylonitrile	9010-76-8	150,000	$[-CH_2CH(Cl)-]_x [-CH_2CH(CN)-]_y$
6.3.5	poly(vinylidene fluoride)	24937-79-9	180,000	$[-CH_2CF_2-]_n$
6.3.7	polytetrafluoroethylene (PTFE)	9002-84-0		$(-CF_2CF_2-)_n$
6.3.8	poly(chlorotrifluoroethylene)	9002-83-9		$[-CF_2CF(Cl)-]_n$
6.3.9	poly(ethylene- <i>alt</i> -chlorotrifluoroethylene)	25101-45-5		$[-CH_2CH_2CF(Cl)CF_2-]_n$
6.3.10	polypropylene chlorinated 32 wt % chlorine	68442-33-1		$[-CX(CX_3)CX_2-]_n$ X = H or Cl
6.3.12	poly(vinylidene fluoride-co-hexafluoro-propylene)	9011-17-0	455,000	$(-CH_2CF_2-)_x [-CF_2CF(CF_3)-]_y$
6.4.1	poly(4-chlorostyrene)	24991-47-7	75,000	$[-CH_2CH(C_6H_4Cl)-]_n$
6.4.2	poly(vinyl-benzyl chloride) 3 and 4 subst. 60/40	121961-20-4	100,000	$[-CH_2CH(C_6H_4CH_2Cl)-]_n$
6.5.2	poly(vinyl alcohol)	9002-89-5	89,000-98,000	$[-CH_2CH(OH)-]_n$
6.5.3	poly(methyl vinyl ether)	9003-09-2		$[-CH_2CH(OCH_3)-]_n$
6.5.4	poly(isobutyl vinyl ether)	9003-44-5		$\{-CH_2CH[OCH_2CH(CH_3)_2]-\}_n$
6.5.5	of poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate)	27360-07-2	50,000-80,000	$\{-CH_2CH[C(O)CH_3]-\}_n$
6.5.6	poly(vinyl methyl ketone)	25038-87-3	500,000	$\{-CH_2CH[C(O)CH_3]-\}_n$
6.5.9	poly(vinyl phenyl ketone)	768-03-6		$\{-CH_2CH[C(O)C_6H_5]-\}_n$
6.5.10	poly(vinyl acetate)	9003-20-7	200,000	$[-CH_2CH(COOCH_3)-]_n$
6.5.11	poly(2-vinylpyridine)	25014-15-7	5,000	$[-CH_2CH(2-C_5H_4N)-]_n$
6.5.13	poly(4-vinylpyridine)	25232-41-1	60,000	$[-CH_2CH(4-C_5H_4N)-]_n$

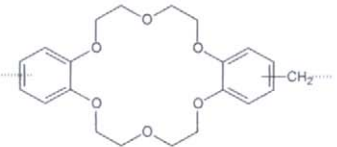
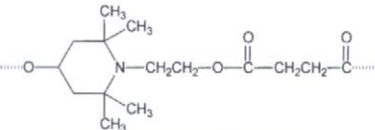
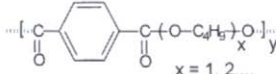
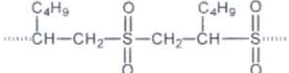
List of Pyrograms of Various Polymers (continued)

Figure	Polymer name	CAS#	M _w	Structure
6.5.14	poly(N-vinyl-2-pyrrolidone) (cross-linked)	25249-54-1		
6.6.1	poly(4-vinylphenol) or poly(4-hydroxystyrene)	24979-70-2	8,000	$[-CH_2CH(C_6H_4OH)-]_n$
6.6.2	poly(4-vinylphenol) or poly(4-hydroxystyrene) silylated	24979-70-2	8,000	$[-CH_2CH(C_6H_4OH)-]_n$
6.6.3	poly(4-styrenesulfonic acid)	28210-41-5		$[-CH_2CH(C_6H_4-SO_3H)-]_n$
6.7.2	poly(acrylic acid)	9003-01-4	1,000,000	$[-CH_2CH(COOH)-]_n$
6.7.4	poly(acrylic acid) TMAH	9003-01-4	1,000,000	$[-CH_2CH(COOH)-]_n$
6.7.7	poly(methyl acrylate)	9003-21-8	30,000	$[-CH_2CH(COOCH_3)-]_n$
6.7.8	poly(butyl acrylate)	9003-49-0	60,000	$\{-CH_2CH[CO_2(CH_2)_3CH_3]-\}_n$
6.7.10	poly(2-ethylhexyl acrylate)	9003-77-4	92,000	$\{-CH_2CH[COOCH_2CH(C_2H_5)(CH_2)_3CH_3]-\}_n$
6.7.13	poly(acrylic acid-co-maleic acid)	29132-58-9	3,000	$[-CH_2CH(COOH)-]_x[-CH(COOH)-CH(COOH)-]_y$
6.7.14	copolymer butyl acrylate, allyl, methyl and 3- (dimethoxymethylsilyl)- propyl methacrylates interpenetrated with cyclic dimethylsiloxane	143106-82-5		
6.7.15	polyacrylamide	9003-06-9	10,000	$[-CH_2CH(CONH_2)-]_n$
6.7.17	poly(acrylic acid) and polyacrylamide (window)	9003-01-4 and 9003-06-9	1,000,000 and 10,000	$[-CH_2CH(COOH)-]_n$ and $[-CH_2CH(CONH_2)-]_n$
6.7.18	poly(N-isopropylacrylamide)	25189-55-3	20,000– 25,000	$\{-CH_2CH[CONH(i-C_3H_7)]-\}_n$
6.7.21	poly(acrylamide-co-acrylic acid) 1.5 wt % acrylic acid	9003-06-9	15,000,000	$[-CH_2CH(CONH_2)-]_x[CH_2CH(COOH)-]_y$
6.7.22	poly(acrylic acid-co- acrylamide) potassium salt crosslinked	90363-65-8		$[-CH_2CH(COOM)-]_x[CH_2CH(CONH_2)-]_y$ M=H, K
6.7.23	polyacrylonitrile	25014-41-9	86,200	$[-CH_2CH(CN)-]_n$
6.7.24	poly(acrylonitrile-co-methyl acrylate)	24968-79-4		$[-CH_2CH(CN)-]_x[CH_2CH(COOCH_3)-]_y$
6.7.25	poly(acrylonitrile-co- butadiene) 19–22 wt % acrylonitrile	9003-18-3		$[-CH_2CH(CN)-]_x[-CH_2CH=CHCH_2-]_y$
6.7.26	poly(acrylonitrile-co- butadiene-co-styrene) high butadiene	9003-56-9		$\cdots(-CH_2-CH-)_x(CH_2-CH=CH-CH_2-)_y(-CH_2-CH-)_z\cdots$ 
6.7.27	poly(methyl methacrylate)	9011-14-7	15,000	$[-CH_2C(CH_3)(COOCH_3)-]_n$
6.7.31	poly(ethyl methacrylate)	9003-42-3	515,000	$[-CH_2C(CH_3)(COOC_2H_5)-]_n$
6.7.33	poly(n-butyl methacrylate)	9003-63-8	320,000	$\{-CH_2C(CH_3)[CO_2(CH_2)_3CH_3]-\}_n$
6.7.34	poly(isobutyl methacrylate)	9011-15-8	300,000	$\{-CH_2C(CH_3)[COOCH_2CH(CH_3)_2]-\}_n$
6.7.35	poly(lauryl methacrylate)	25719-52-2	470,000	$\{-CH_2C(CH_3)[COO(CH_2)_{11}CH_3]-\}_n$
6.7.41	poly(2-hydroxyethyl methacrylate)	25249-16-5	20,000	$[-CH_2C(CH_3)(COOCH_2CH_2OH)-]_n$
6.7.42	poly(butyl methacrylate-co- methyl methacrylate) monomer ratio butyl/methyl 1.4/1.0	25608-33-7	100,000	$[-CH_2C(CH_3)(COOCH_3)-]_x$ $[CH_2C(CH_3)(COOC_4H_9)-]_y$

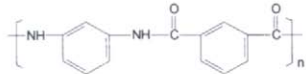
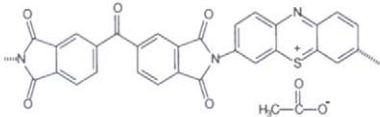
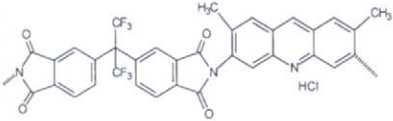
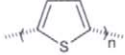
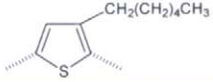
List of Pyrograms of Various Polymers (continued)

Figure	Polymer name	CAS#	M _w	Structure
7.1.1	polybutadiene (<i>cis</i>)	40022-03-5	2,000,000 3,000,000	$(-\text{CH}_2\text{CH}=\text{CHCH}_2-)_n$
7.1.2	polybutadiene, phenyl terminated 45% vinyl	106-99-0	\overline{M}_n 1,000	$\text{C}_6\text{H}_5-(\text{CH}_2\text{CH}=\text{CHCH}_2-)_n-\text{C}_6\text{H}_5$
7.1.3	polyisoprene (<i>cis</i>)	104389-31-3	38,000	$[-\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2-]_n$
7.1.4	polyisoprene (<i>cis</i>) (window)	104389-31-3	38,000	$[-\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2-]_n$
7.1.5	polyisoprene (<i>cis</i>) (window)	104389-31-3	38,000	$[-\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2-]_n$
7.1.6	polyisoprene-graft-maleic anhydride	139948-75-7	25,000	
7.3.1	polychloroprene 10% <i>cis</i> , 85% <i>trans</i>	910-98-4		$[-\text{CH}_2\text{CH}=\text{C}(\text{Cl})\text{CH}_2-]_n$
8.3.1	poly[(phenyl-co-formaldehyde) or phenol formaldehyde resin			see page 467
8.3.2	poly[(phenyl glycidyl ether)-co-formaldehyde] or phenol formaldehyde polymer oxirane methanol ether; average 2.2 epoxide groups per molecule.	28064-14-4	\overline{M}_n 345	
8.3.3	poly[(o-cresyl glycidyl ether)-co-formaldehyde]	29690-82-2	\overline{M}_n 1,080	
9.1.1	poly(ethylene glycol)	25322-68-3	\overline{M}_n 1,000	$\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$
9.1.2	poly(ethylene glycol)	25322-68-3	\overline{M}_n 10,000	$\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$
9.1.5	poly(ethylene oxide) (BHT inhibitor)	25322-68-3	300,000	$(-\text{CH}_2\text{CH}_2\text{O}-)_n$
9.1.6	poly(oxyethylene)(23) lauryl ether (Brij 35)			
9.1.8	poly(ethyleneglycol) dimethacrylate (monomethyl ether hydroquinone inhibitor)	25852-47-5	\overline{M}_n 875	$\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CO}(\text{OCH}_2\text{CH}_2)_n\text{OOC}(\text{CH}_3)=\text{CH}_2$
9.1.9	polyethylene-block-poly(ethylene glycol) (20% wt. ethylene oxide)	97953-22-5	\overline{M}_n 575	$\text{CH}_3\text{CH}_2(\text{CH}_2\text{CH}_2)_x(\text{OCH}_2\text{CH}_2)_y\text{OH}$
9.1.10	poly(propylene glycol) or poly(propylene oxide)	25322-69-4	\overline{M}_n 345	$\text{H}[-\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2-]_n-\text{OH}$
9.1.11	poly(propylene glycol) or poly(propylene oxide) (window)	25322-69-4	\overline{M}_n 345	$\text{H}[-\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2-]_n-\text{OH}$
9.1.13	polytetrahydrofuran [α -hydro- ω -hydroxy-poly(oxy-1,4-butandiyl)]	25190-06-1	\overline{M}_n 250	$\text{H}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2)_n\text{OH}$

List of Pyrograms of Various Polymers (continued)

Figure	Polymer name	CAS#	M _w	Structure
9.1.15	poly[(dibenzo-18-crown-6)-co-formaldehyde]	53660-42-7		
9.1.17	poly(2,6-dimethyl-1,4-phenylene oxide)	25134-01-4	244,000	$[\text{C}_6\text{H}_2(\text{CH}_3)_2\text{O}]_n$
9.1.18	polyepichlorohydrin	24969-06-0	700,000	$[-\text{CH}(\text{CH}_2\text{Cl})\text{CH}_2\text{O}]_n$
9.1.19	poly(hexafluoropropylene oxide)	60164-51-4		$\text{C}_2\text{F}_5[-\text{OCF}_2\text{CF}(\text{CF}_3)]_n\text{F}$
9.1.20	poly(hexafluoropropylene oxide) at 850	60164-51-4	at 850° C	$\text{C}_2\text{F}_5[-\text{OCF}_2\text{CF}(\text{CF}_3)]_n\text{F}$
10.1.1	poly(L-lactide)	33135-50-1	10,000-150,000	$[-\text{OCH}(\text{CH}_3)\text{CO}]_n$
10.1.2	polycaprolactone	24980-41-4	14,000	$[-\text{O}(\text{CH}_2)_5\text{CO}]_n$
10.1.4	poly[di(ethylene glycol) adipate]	9010-89-3		$[-\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}_2\text{C}(\text{CH}_2)_4\text{CO}]_n$
10.1.6	poly(4-hydroxy-2,2,6,6-tetramethyl-1-piperidinoethanol- <i>alt</i> -1,4-butandioic acid)	65447-77-0	\underline{M}_n 3500	
10.1.11	poly(ethylene terephthalate)	25038-59-9	\underline{M}_x 18,000	$(-\text{OCH}_2\text{CH}_2\text{OOC}\text{C}_6\text{H}_4-4-\text{CO}-)_n$
10.1.12	poly(1,4-butylene terephthalate)	24968-12-5	\underline{M}_x 38,000	$[-\text{O}(\text{CH}_2)_4\text{O}_2\text{C}\text{C}_6\text{H}_4-4-\text{CO}]_n$
10.1.15	poly[butylene terephthalate-co-poly(butylene glycol) terephthalate]			 $x = 1, 2, \dots$
11.1.1	poly(bisphenol A carbonate)	25037-45-0	29,000	$[-\text{OC}_6\text{H}_4-4-\text{C}(\text{CH}_3)_2\text{C}_6\text{H}_4-4-\text{OC}(\text{O})-]_n$
11.1.2	poly(hexamethylene carbonate) diol	61630-98-6	\underline{M}_n 860	$\text{HO}[-\text{CH}_2(\text{CH}_2)_4\text{CH}_2\text{OCOO}]_n\text{CH}_2(\text{CH}_2)_4\text{CH}_2\text{OH}$
11.1.6	copolymer of poly(1,6-hexyl-1,2-ethyl carbonate)diol, 4,4'-methylenebis(phenyl isocyanate) and 1,4-butandiol. (soft)		264,000	see page 567
11.1.7	copolymer of poly(1,6-hexyl-1,2-ethyl carbonate)diol, 4,4'-methylenebis(phenyl isocyanate) and 1,4-butandiol. (hard)		237,000	see page 567
12.1.2	poly(1,4-phenylene sulfide) at 850° C	25212-74-2		$(-\text{C}_6\text{H}_4-\text{S}-)_n$
12.2.1	poly(1-hexene-sulfone)	34903-07-6		

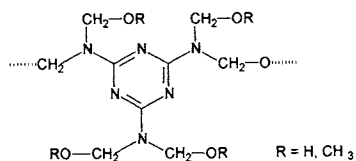
List of Pyrograms of Various Polymers (continued)

Figure	Polymer name	CAS#	M _w	Structure
12.2.2	poly(oxy-1,4-phenylene-sulfonyl-1,4-phenylene) or poly(1,4-phenylene ether sulfone) at 850° C	25667-42-9		$(-\text{OC}_6\text{H}_4-\text{SO}_2-\text{C}_6\text{H}_4-)_n$
12.2.3	polysulfone or bisphenol A ethersulfone at 850° C	25135-51-7	67,000	$[-\text{C}_6\text{H}_4-4-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-4-\text{O}-\text{C}_6\text{H}_4-4-\text{SO}_2-\text{C}_6\text{H}_4-4-\text{O}-]_n$
13.1.1	polyethyleneimine (Mix of linear and branched chains)	29320-38-5	M _n 423	$\text{H}(-\text{NHCH}_2\text{CH}_2-)_n\text{NH}_2$
13.3.2	polycaprolactam or Nylon 6	25038-54-4		$[-\text{NH}(\text{CH}_2)_5\text{CO}-]_n$
13.3.3	polycaprolactam or Nylon 6 (window)	25038-54-4		$[-\text{NH}(\text{CH}_2)_5\text{CO}-]_n$
13.3.4	Nylon 12 polydodecylactam	24937-16-4		$[-\text{NH}(\text{CH}_2)_{11}\text{CO}-]_n$
13.3.6	poly(hexamethylene adipamide) or nylon 6,6	32131-17-2		$[\text{NH}(\text{CH}_2)_6\text{NHCO}(\text{CH}_2)_4\text{CO}-]_n$
13.3.7	poly(hexamethylene sebacamide)	9008-66-6		$[\text{NH}(\text{CH}_2)_6\text{NHCO}(\text{CH}_2)_8\text{CO}-]_n$
13.3.9	Nomex at 850° C			
13.4.1	poly(3,3',4,4'-benzophenonetetracarboxylic dianhydride-alt-thionin) at 850° C			
13.4.3	poly[4,4'-hexafluoroisopropylidene)-diphthalic anhydride-alt-acridine yellow G] HCl at 850° C			
14.1.1	poly[4,4'-methylenebis(phenyl isocyanate)-alt-butandiol/polytetrahydrofuran]	9018-04-6		$\cdots\{\text{R}-\text{O}-(\text{CH}_2)_4-\text{O}\}_x\{\text{R}-\text{O}-(\text{CH}_2)_4-\text{O}\}_y\cdots$ $\text{R} = \text{---}\text{C}(=\text{O})\text{NH}-\text{C}_6\text{H}_4-\text{CH}_2-\text{C}_6\text{H}_4-\text{NH}-\text{C}(=\text{O})\text{---}$
15.1.2	poly(thiophene-2,5-diyl), Br terminated at 850° C	110-02-1		
15.1.4	poly(3-hexylthiophene-2,5-diyl) regioregular at 850° C	104934-50-1	87,000	

List of Pyrograms of Various Polymers (continued)

15.3.1 poly(melamine-co-
formaldehyde), methylated,
molar ratio
melamine/formaldehyde/
methoxy 1/5.8/5.0

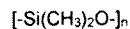
68002-20-0

 \overline{M}_n 511

16.1.1 poly(dimethylsiloxane)

9016-00-6

95,000



16.1.2 poly(dimethylsiloxane-co-
methylphenylsiloxane) 1/1
mole ratio

63148-52-7



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